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## I. INTRODUCTION

At the present time there is a widespread interest in the chemistry of boron. Especially is this true in the field of organo-boron compounds, for boron has been found to possess the property of forming ring and chain compounds with itself or with certain organic groups.

Many organo-boron compounds may be prepared by standard organic reactions. Interest has developed in the possible electrochemical formation of boron-containing organic compounds. A considerable saving in materials of construction, power, and reaction time may result if these syntheses are performed electrochemically.

The formation of organo-boron compounds may be accomplished through the anodic formation of a free alkyl radical by electrolyzing a solution of an alkyl alkali compound such as lithium ethyl, along with a simultaneous electrolysis of an alkali borohydride. The deposition of the free alkyl radical in the presence of the borohydride radical may result in a reaction between the two.

The purpose of this investigation was to study the electrolysis of diethyl ether solutions of lithium methyl, lithium ethyl, lithium butyl, or ethyl magnesium bromide in the presence of lithium borohydride.

## II. LITERATURE REVIEW

In this section is contained a review of the literature that was pertinent to this investigation. The review is divided into the following sections: free alkyl radicals, organo-metallic compounds, the grignard reagent, metal borohydrides, and organo-boron compounds.

### Free Alkyl Radicals

The history, properties and reactions of the free alkyl radicals are discussed in the following section.

Early History of Free Radicals. In 1832, Liebig and Wohler<sup>(44)</sup>, starting with benzaldehyde, converted it into a series of related compounds, all containing the group  $C_7 H_5 O$ . A short time later, Laurent<sup>(41)</sup> claimed to have prepared the free benzoyl radical, while in actuality, he had prepared dibenzoyl or benzil. Liebig<sup>(43)</sup> showed that alcohol, its esters and ether could all be considered as derivatives of the radical  $C_2 H_5$  and predicted the isolation of free alkyl radicals by the action of potassium on their chlorides or iodides. Frankland<sup>(15)</sup> heated ethyl iodide and metallic zinc to  $150^{\circ}C$  in a sealed glass

tube. On opening the tube, he found a gas of empirical formula  $C_2 H_5$ , which he considered the free ethyl radical. Actually, of course, he had prepared butane. At the same time Kolbe<sup>(3)</sup> electrolyzed acetic acid and obtained a gas which he regarded as free methyl (in reality ethane).

From 1860 to 1900 the postulate of the quadrivalence of carbon was fully accepted and served as the entire basis for the development of organic chemistry during this period. This development discouraged any further interest in free radicals.

In 1900 interest in free radicals was revived. However, it was then clear that the methods of classical organic chemistry were powerless to obtain aliphatic radicals in the free state or even to demonstrate with certainty their existence as fugitive intermediates in a chemical reaction.

Early Experiments. The discovery and study of the free methyl group by Paneth and Hofeditz<sup>(48)</sup> in 1929 gave a great stimulus to the interest in free radicals. These authors showed that lead tetramethyl carried in a stream of pure hydrogen at pressures of one or two millimeters of mercury can be decomposed by heating, into metallic lead and free methyl groups. The free methyl groups are carried rapidly out of the heated

zone and can be made to combine with a variety of metals when these are distilled into the walls in the form of metallic mirrors. The organo metallic products formed were shown to consist only of the methyl derivative. The free methyl groups combine rapidly after leaving the furnace, and they have a half life of only 0.006 second.

Paneth and his coworkers mention a number of metals, i. e., lead, antimony, zinc, cadmium and tellurium, which react readily with free radicals.

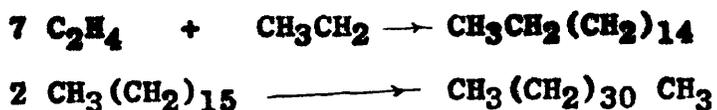
Identification of Free Radicals. Paneth and Hofeditz<sup>(48)</sup> identified the free methyl group produced in their experiments by combining it with zinc; zinc dimethyl was identified by its melting and boiling points, and from its spontaneous combustion in air with the separation of zinc oxide. Paneth and Lautsch<sup>(49)</sup> identified the free ethyl group prepared from lead tetraethyl in a similar manner. They obtained final identification through the formation of the compound  $C_2H_5-O-O-Zn-C_2H_5$  as the result of partial oxidation of the product. This compound precipitates as a white powder which can be readily hydrolyzed and the ethyl alcohol formed identified by the iodoform test.

Properties of Free Radicals. The most distinctive property of free radicals is their short life. The

first measurements of the half life were made by Paneth and Hofeditz (48). Methyl groups were prepared by decomposing lead tetramethyl in a current of hydrogen and the time of disappearance of a standard antimony mirror was used as a measure of the concentration of the radicals. Mirrors were deposited at different measured intervals from the furnace in which the radicals were formed. The times of disappearance of the mirrors gave a relative measure of the concentration of the radicals at the different points, knowing the rate of flow of hydrogen in the tube.

Reactions of Free Radicals With Olefins. In the work of Taylor and Jones (64) varying proportions of free radicals (ethyl and methyl groups) were introduced into pure ethylene or into mixtures of ethylene and hydrogen. The total pressure was kept at half an atmosphere and the temperature was in the range of 250-300°C, in which range ethylene neither polymerizes nor reacts with hydrogen. The radicals were furnished by the decomposition of lead or mercury alkyls, which break down to the metal and the free radical at that temperature. In one experiment it was found that when pure ethylene was used each ethyl radical added caused seven molecules of ethylene to disappear from the

reaction. These were recovered in the form of an oil, presumably produced by



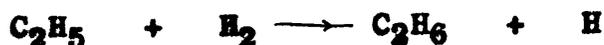
This reaction involves the addition of 7 ethylene molecules to an ethyl free radical, followed by combination of disproportionation of the larger molecule.

Cramer<sup>(8)</sup> has studied the reactions of free ethyl groups with ethylene in the liquid phase, with lead tetraethyl used as a source of ethyl groups. The results of Cramer's work indicated that the decomposition of tetraethyl lead involves the disproportionating reaction of the ethyl radical



Interaction of Radicals With Organic Molecules.

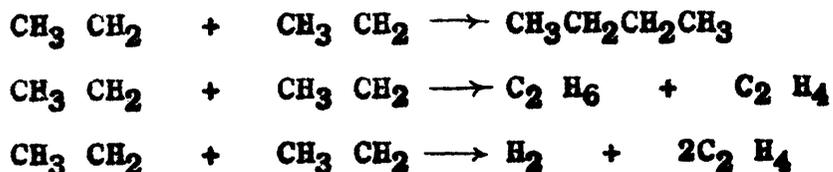
Leermakers<sup>(42)</sup> has decomposed lead tetraethyl in the presence of hydrogen and has found that the reaction



has an activation energy of 15 calories or more. In the interaction of radicals and organic molecules it is found that all reactions involving the rupture of the carbon skeleton of the substrate by the free radicals have a sufficiently high activation energy that they can be neglected in comparison with the

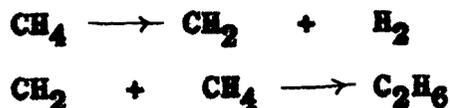
reactions between the free radicals and the hydrogen atoms attached to the carbon skeleton<sup>(54)</sup>.

Interaction of Radicals With Each Other. This type of reaction may be illustrated with reference to the ethyl radical as follows:



These reactions are strongly exothermic (40-80 calories) so they may be expected to occur with little or no energy of activation. In a paper by Rice and Herzfeld<sup>(53)</sup> an activation energy of 8 calories has been assigned to all mechanism to agree with the experimental results.

Decomposition of Methane. The decomposition of methane, according to Kassel<sup>(40)</sup> consists of two reactions

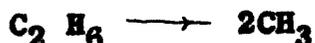


However, it is possible that the primary dissociation into a hydrogen molecule and the methylene group may be followed by the reaction

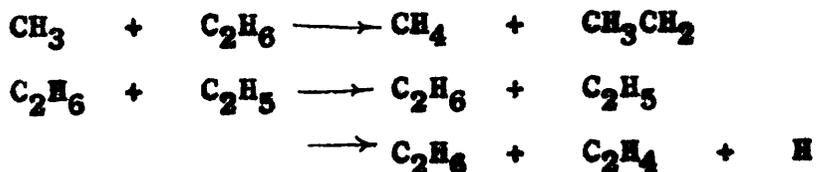


Decomposition of Ethane. By the free radical mechanism, the primary decomposition of ethane

produces two methyl groups by rupture of the C-C bond.



These radicals then react with the surrounding ethane to form methane and ethyl groups which finally decompose to ethylene and atomic hydrogen.



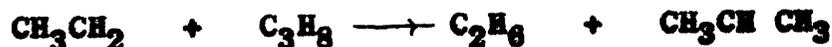
Decomposition of Propane. The primary decomposition of propane<sup>(54)</sup> yields methyl and ethyl radicals by rupture of the C-C bond.



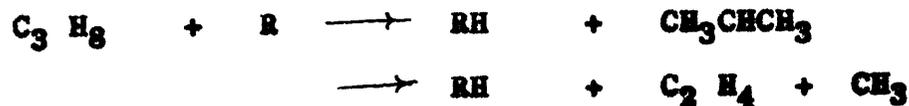
this is followed by



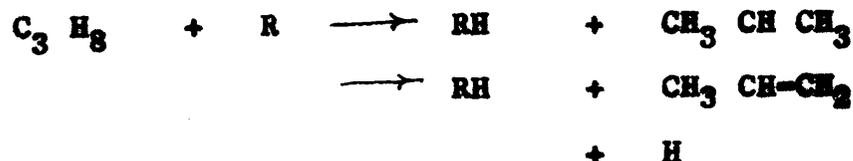
or



followed by



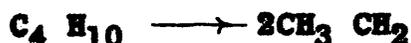
or



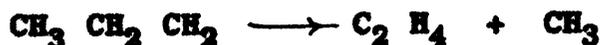
Decomposition of n-Butane. The decomposition of butane may be represented by a primary reaction of either



or



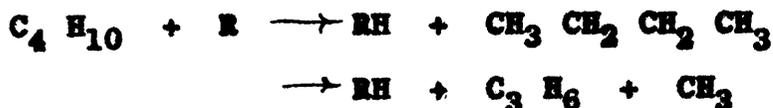
followed by



then



or



Four Basic Reactions of Radicals With Organic Molecules. First of the four basic reactions is the addition of a radical to an unsaturated organic molecule as follows:



These reactions are important only at relatively low temperatures (below 300°C) because of their instability and low activation energy.

The second type of reaction is that of removal of a hydrogen atom from an organic molecule and occurs

above 400°C.



or



The third type is the rupture of an organic molecule by a radical as in the following reaction:



The fourth type is the recombination or interaction of radicals. This can be illustrated as follows:



#### Production of Free Radicals by Electrochemical

Means. Free alkyl radicals have been produced by electrochemical methods in the electrolysis of the grignard reagent in ether solution, by the electrolysis of alkali alkyls in diethyl zinc, and by the electrolysis of organic acids. It was found that in the case of the electrolysis of the grignard reagent in ether solution, the organic free radicals thus produced may react by (1) coupling, (2) by disproportionation, or (3) by the removal of hydrogen from the ether solvent.

Electrolytic Studies of Methyl and Ethyl Magnesium Halides. Evans and Nelson<sup>(13)</sup> studied the effect of the resistance of ethyl ether and benzene when ethyl magnesium bromide was added to them. The results obtained are given in Table I, page 12. Evans and

TABLE I

Comparative Electrolytic Resistance of Cells Containing  
Ethyl Magnesium Bromide<sup>a</sup>

Solution	Resistance ohms
Ether	above $1 \times 10^7$
Benzene	above $1 \times 10^7$
Ether, containing ethyl bromide	above $1 \times 10^7$
Ether, benzene containing ethyl bromide	above $1 \times 10^7$
Ether, containing 1.2 gm Mg as grig/100 ml	$7.1 \times 10^3$
Ether, containing 0.6 gm Mg as grig/100 ml	$2.4 \times 10^4$
Ether, containing 0.3 gm Mg as grig/100 ml	$1.0 \times 10^5$
0.02 M aqueous KCl solution	$1.26 \times 10^2$

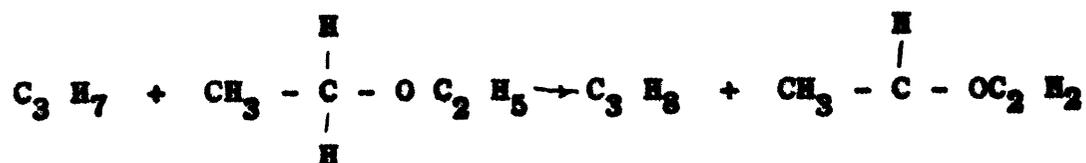
a. Evans, W. V., and J. M. Nelson: The Electromotive Force  
Developed in Cells Containing Non Aqueous Liquids,  
J. Am. Chem. Soc., 39, 82 (1917)

Lee<sup>(12)</sup>, however, were the first to identify quantitatively the anodic products of the electrolysis of these grignards. The results of their investigations show that the major anode products of this electrolysis of these ethyl containing grignards are ethane and ethylene, with about one per cent hydrogen present. However, in the electrolysis of the methyl grignards, the anode products vary with concentration. At high concentrations, ethane is the chief product, while at low concentrations more methane and unsaturated products, such as isobutylene and ethylene are formed. The reactions for the disproportionation of the free alkyl radical proposed by Evans and Lee are

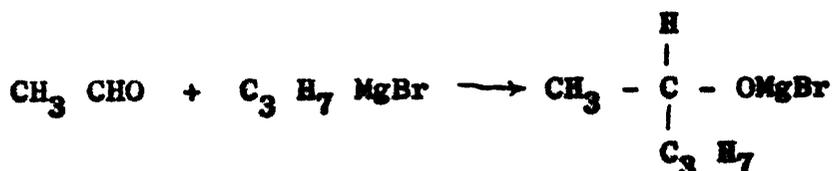
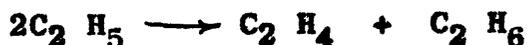


Later, Evans and Field<sup>(10,11)</sup> working with methyl magnesium bromide, chloride, and iodide, determined that, in addition to the predominate anode products, methane and ethane, one to four per cent ethylene and carbon dioxide were formed. These definitely were produced from the ether solvent. Therefore, the formation of alkyls by the reaction of the free radical with the hydrogen from the ether is another reaction to be considered.

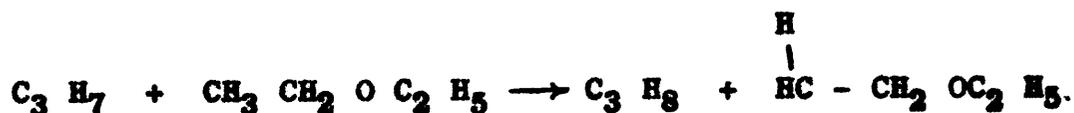
Electrolytic Studies of Propyl Grignards. Evans and Braithwaite<sup>(9)</sup> studied the electrolysis of n-propyl and isopropyl magnesium bromide in ethyl ether. The products of this electrolysis were determined and the proposed reactions are:



for the reaction of the alkyl radical with ether

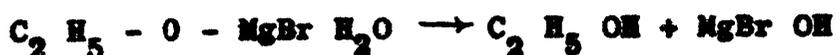
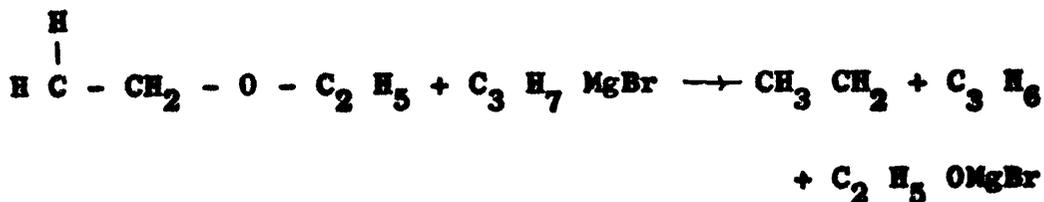


and with the  $\beta$  hydrogen of the ether



In this mechanism, it is observed that the final reactions were hydrolyzed before the liquid products.

were separated. By balanced equations



Electrolysis of Aromatic Grignards. Goddum and French<sup>(27)</sup> were the first to study the anode products of the electrolysis of aromatic magnesium halides. The grignards studied were p-tolyl magnesium chloride, and benzil magnesium bromide. The products obtained are given in Table II, page 16.

Evans and his coworkers<sup>(14)</sup> performed their investigation to study the short lived aryl radicals. Phenyl, p-tolyl, p-chlorophenyl, and benzylmagnesium bromides were electrolyzed. They found that neither coupling nor disproportionation is the chief reaction of the free aryl radicals. However, the products formed can be explained if the reactions are assumed to be (1) coupling, followed by an attack by radicals upon the coupled product, or (2) an attack by radicals on the ether solvent.

TABLE II

Products of Electrolysis of Aromatic Magnesium Halides <sup>a</sup>

Experiment no	Grignard studied	Conc. of grignard moles per liter	Products of electrolysis	Equivalents of electricity
1	$C_6H_5CH_2MgCl$	1.01	$C_6H_5CH-CH-C_6H_5$	0.2667
2	$C_6H_5CH_2MgCl$	0.802	$MgCl_2$ $Mg_2$	0.2864
3	$C_6H_5MgBr$	1.542	$C_6H_5C_6H_5$	0.2294
4	"	1.70	$MgBr_2$ $Mg_2$	0.3213
5	"	1.73		-
6	"	1.00		-
7	"	1.43		-
8	"	1.43		-

a. Goddum, L. W. and H. E. French: The Electrolysis of Grignard Solutions, J. Am. Chem. Soc., 49, 1295 (1927)

Electrolysis of Alkali Alkyls. Electrolysis of sodium ethyl in diethyl zinc<sup>(31,32,33)</sup> gave zinc at the cathode and a mixture of ethane and ethylene at the anode. Lithium ethyl showed a conductance 1/28 that of sodium ethyl in diethyl zinc. The molar conductances of various alkali alkyls in diethyl zinc are 0.13 for lithium ethyl, 4.01 for sodium ethyl, 6.49 for potassium ethyl, and 9.39 for rubidium ethyl. Dilution of the zinc diethyl - lithium ethyl solution with zinc diethyl caused separation into two layers, the lower layer conducting. The cathode product of the electrolysis of sodium ethyl in diethyl zinc was pure zinc. The decomposition potential was 0.1 volt. The end result of this electrolysis is an indirect decomposition of the diethyl zinc and there is evidence that only sodium and ethyl ions exist in solution. Lithium methyl was miscible in all proportions with diethyl zinc and conducted better than sodium ethyl; however, a solution of lithium ethyl in benzene was nonconductive.

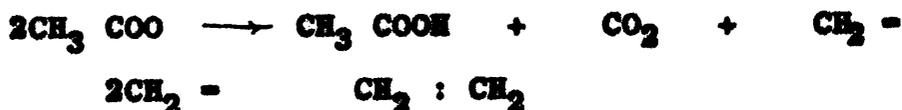
Kolbe Synthesis. Salts of organic acids of the type  $\text{RCOOM}^{(3)}$  in water solution ionize into  $\text{RCOO}^-$  and  $\text{M}^+$ . These ions carry the current when a solution of the salt is electrolyzed. In the case of potassium acetate, an electrolysis of this solution

showed at the anode a mixture of carbon dioxide, hydrogen, ethane, ethylene, and methyl acetate.

Brown and Walker<sup>(4)</sup> postulated the following mechanism for the reaction



and



other mechanisms have been postulated, and in all the formation of a free alkyl radical is present.

### Organo Metallic Compounds

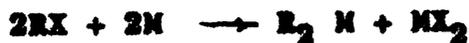
Since the discovery of diethyl zinc by Franklin<sup>(15)</sup> in 1849, organo-metallic compounds have been increasingly valuable in the field of organic chemistry. They have been used chiefly in synthesis and for the study of reaction mechanism.

Preparation of Organo-metallic Compounds. The preparations<sup>(72)</sup> of organo metallic compounds can be classified into three groups.

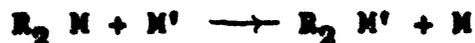
(A) The action of a metal or an alloy of the metal on a halide.



or

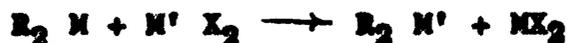


(B) The action of a metal on the organo-metallic compound prepared from another metal



where M' is generally of a higher potential or above M in the electromotive series.

(C) The action of a metal halide on the organo-metallic compound prepared from another metal.

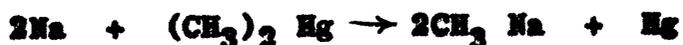


M' is generally below M in the electromagnetic series.

The organo-metallic compounds of the group II elements, especially those of magnesium, zinc, and cadmium are particularly interesting. Systematic studies of these compounds by Moller<sup>(47)</sup>, Casson<sup>(7)</sup> and other workers have shown the compounds to be invaluable in the synthesis of not only other organic compounds but also the less known organo-metallic compounds.

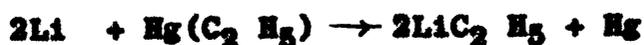
Alkali Alkyls. The simplest organo-alkali compounds are those which could theoretically be derived from the paraffin hydrocarbons by the substitution of a single atom of hydrogen by an alkali metal atom. These are termed the alkali alkyls. These cannot, in general, be prepared by direct substitution.

Preparation of Alkali Alkyls. The most general preparation of these compounds is by the action of alkali metals on the corresponding mercury alkyls (56). This reaction must be carried out under rigid exclusion of air and moisture. The preparation of sodium methyl may be represented as follows:



To separate the sodium methyl, which forms a solid crust on the amalgam of mercury and sodium, and which may not be dissolved in any known solvent without decomposition, the reaction vessel is placed in a freezing mixture and shaken until the product is reduced to a powder. The product is then washed. Sodium methyl is a white powder which explodes in air.

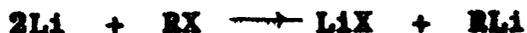
Lithium ethyl was obtained from diethyl mercury and lithium in benzene



the product was soluble and was purified by crystallization from the solvent. It has been obtained in transparent crystals having the form of six sided plates. It melted at 95°C under nitrogen. It was soluble in benzene, benzine, and gasoline, but it reacted slowly with ether and ignited spontaneously in air. (62)

Ziegler (73,74,75,76) and others (77,78,79) have found that in many cases the lithium alkyls may be

prepared by the action of the metal on the corresponding alkyl halide.



The possibility was based on the relative solubility of these organo-alkali compounds toward alkyl halides. The alkyl chlorides are preferable to the bromides, and the iodides cannot generally be used. Benzene and cyclohexane were more suitable as solvents than ether, which reacted slowly with the alkali alkyl.

The work of Ziegler has been perfected and refined by Gilman<sup>(20,25,26)</sup> and the preparations and reactions of the lithium alkyls have been studied extensively<sup>(18,19,22,23)</sup>. Reaction time<sup>(26)</sup>, effect of the tarnishing of the lithium<sup>(26)</sup>, information about the optimum size of the lithium<sup>(25)</sup>, and yields<sup>(22,25)</sup> are given. Also a further improved procedure for the production of lithium alkyls in 88 to 98 per cent yield in 0.5 to 1.0 mole quantities was given by Perine and Rappaport<sup>(51)</sup>. The improvement was brought about by the use of lithium sand prepared by cooling molten lithium in petrolatum and by the use of a filter device which permits the operation of the experiment in an inert atmosphere of helium.

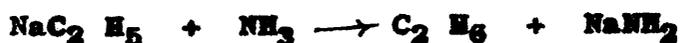
Talalaeva and Kocheshkov<sup>(61,62)</sup> obtained pure crystalline lithium ethyl by the reaction of lithium

metal with ethyl bromide and the lithium ethyl thus produced was separated from the by-product lithium bromide by differing solubilities in benzene, hexane or isopentane. The yields obtained by this reaction reached 65 per cent. The solubilities of lithium ethyl in several solvents were also determined. Lithium ethyl was found to be soluble in pentane, one gram per 100 grams, at 18°C, in isopentane three grams per 100 grams, at 16°C, in hexane 9.5 grams per 100 grams at 55°C, and in benzene 7 grams per 100 grams at 16°C.

Preparation of Lithium Butyl at Low Temperatures.

By carrying out the reaction of lithium metal with alkyl halides at -10°C, Gilman and coworkers<sup>(20)</sup> found that the yields obtained at room temperature (50 to 65 per cent) could be considerably improved. Yields of approximately 78 per cent were attained by these low temperature preparations. Lithium wire was used in all these reactions.

Sodium and Potassium Alkyls. The potassium and sodium alkyls<sup>(72)</sup> were perhaps the most highly reactive compounds ever isolated. Sodium ethyl, for example, was not only spontaneously inflammable in air but was also instantly decomposed by water and ammonia,



and entered into reaction with all classes of organic compounds, except the paraffins.

Physical Properties of Organo-Alkali Compounds.

The reactivity of the organo-alkali compounds suggested a marked difference between their constitution and that of the more stable organic molecules. In consideration of the electropositive nature of the alkali metals and the amphoteric nature of the organic radicals, it was expected that their union would produce polar substances more or less analogous to the alkali metal hydrides.

Experimental confirmation of this view has been sought in a study of the electrical conductivity of these substances, but it has been difficult going, as only certain of the lithium alkyls may be liquified without decomposition and suitable solvents are rare.

When lead anodes were used, a loss in weight approximately equal to the amount corresponding to Faraday's law was observed as a result of the formation of tetraethyl lead<sup>(31,32)</sup>.

The extreme reactivity of the alkali alkyls made it necessary to use special apparatus to prepare them, in which air and moisture were rigidly excluded.

Lithium butyl distilled in a molecular still at  $10^{-4}$  millimeters of mercury at 80 to 90°C. Lithium ethyl sublimed at high vacuum at 70°C to give clear,

shiny crystals. Also the higher lithium alkyls were found to be liquids.

Sodium Alkyls. Sodium alkyls were also produced from alkyl chlorides and sodium at low temperatures in petrolatum. N-butyl, n-oetyl and others have been produced in this way<sup>(56)</sup>.

The sodium alkyls are amorphous powders, insoluble in inert solvents, and which decomposed on heating without melting. When exposed to air, they inflamed immediately, and burned explosively. Inflammability of the compounds decreased with increasing size of the alkyl radical. Sodium methyl, ethyl, propyl and tolyl have been prepared by the method of Schlenk<sup>(56)</sup>.

Solubility of Alkali Alkyls. In general, the sodium and potassium alkyls are insoluble in inert solvents; solution of sodium and potassium alkyls in diethyl zinc, can be effected, however, and these will conduct a current<sup>(32)</sup>. Lithium alkyls, however, are soluble in organic solvents and conduct a current poorly in diethyl zinc. Petroleum ether, diethyl ether, benzene, gasoline, cyclohexane, and skellysolve have been used as solvents for lithium alkyls<sup>(20,25,26)</sup>.

Decomposition of Alkali Alkyls in Ether. The alkali alkyls decomposed at varying rates in methyl and ethyl ether. Sodium ethyl reacted with ether to

form sodium ethylate, ethane, and ethylene<sup>(49)</sup>. Lithium alkyls decomposed 10 to 20 times faster in methyl ether than in ethyl ether<sup>(58)</sup>. In methyl ether the products were lithium methylate, pentane, hexane, and octane.

The organo lithium compound that was the most stable in diethyl ether was methyl lithium<sup>(30)</sup>. A 0.54 normal solution of this compound was found to be 0.14 normal after one year. Tertiary-butyl lithium cleaved ether most rapidly, a 0.14 normal solution decomposing at room temperature in 30 minutes.

Temperature had a marked effect on the rate of decomposition of the lithium alkyls. At 25°C, 18 days were required to cleave a 0.65 normal solution of n-butyl lithium while at 35°C only five and one half days were required.

Aromatic organo lithium compounds cleaved ether more slowly than the aliphatic compounds. While a 0.4 normal solution of n-amyl lithium decomposed by refluxing in ether for four days, a 0.4 normal solution of phenyl lithium when refluxed for 30 days was found to be 0.09 normal.

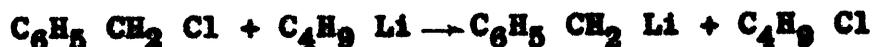
#### Quantitative Analysis of Alkyl Lithium Compounds.

A method for determining the amount of alkyl lithium present was presented by Ziegler<sup>(77)</sup>. The method

consisted of taking two aliquots from the solution to be tested. One aliquot was hydrolyzed to lithium hydroxide. The second was titrated for lithium hydroxide present after the lithium alkyl had been destroyed. The lithium alkyl was destroyed by adding n-butyl bromide and dibenzylmercury. The benzyl lithium formed by reaction of the alkyl lithium and dibenzylmercury was destroyed by butyl bromide.

The quantitative analysis of alkyl lithium was also discussed by Gilman and Haubein<sup>(21)</sup>. In their work, the lithium butyl in diethyl ether was destroyed with benzyl chloride rather than with n-butyl bromide and dibenzylmercury. However, if the lithium alkyl were in petroleum ether, a simple hydrolysis followed by titration by standard acid was sufficient.

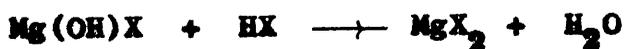
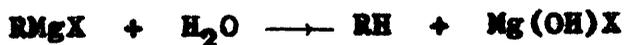
The reaction for the decomposition of the lithium alkyl was assumed to be<sup>(30)</sup>



### The Grignard Reagent

In general, the most important of the organo-metallic compounds are the RMgX, or grignard reagents. A knowledge of the properties of these compounds should provide a useful basis for orienting and correlating the other organo-metallic compounds.

Preparation. The grignard reagent has been readily and conveniently prepared<sup>(50)</sup> in dry ether. Some RX compounds reacted slowly, but by appropriate catalytic devices it has been possible to initiate and accelerate the reaction. The yields were highly satisfactory, and the more frequently used grignard reagents were obtainable in about 90-95 per cent yield. A simple procedure for the quantitative estimation of reactive and moderately reactive organo-metallic compounds was to hydrolyze an aliquot and titrate the basic compound formed with a standard acid<sup>(77)</sup>.



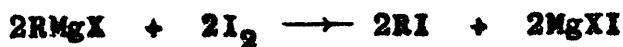
Physical Properties. The grignard compounds are colorless solids which do not melt but decompose at elevated temperatures, first undergoing, in all probability, the following transformation which may be general for all mixed organo-metallic compounds:



The dialkyl magnesium compounds are colorless crystals which can be sublimed at reduced pressures.

Chemical Properties. The grignard reagents were cleaved by hydrogen, active hydrogen compounds, and

halogens (17).



They reacted with oxygen and sulfur as follows (17):



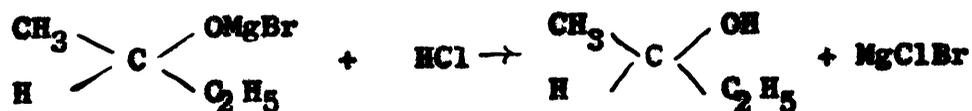
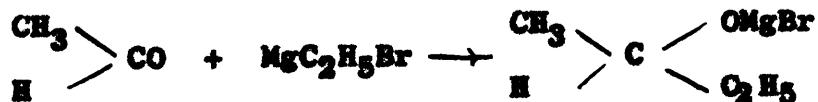
Grignard reagents reacted with those metals which gave more reactive organo-metallic compounds.



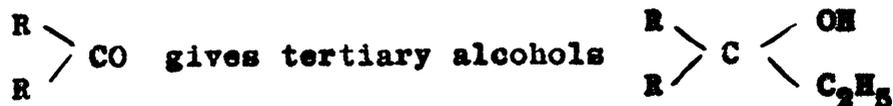
However, the RMgX compounds gave other organo-metallic compounds with those inorganic salts, generally the halides, which form less reactive organo-metallic compounds.



They also reacted with substances containing a carbonyl group (50)



and with ketones



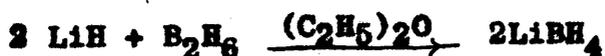
in a similar manner.

### Metal Borohydrides

In this section is contained information on the physical and chemical properties of the metal borohydrides.

Lithium Borohydride. Lithium borohydride<sup>(55)</sup> was reported to be a white crystalline solid, melting at 275°C with slow decomposition. It was stable to dry air<sup>(57, 58)</sup>.

It can be prepared by the following methods<sup>(54)</sup>.



In the latter reaction<sup>(57)</sup> the lithium borohydride was precipitated out of the benzene solution.

Lithium borohydride was found to be soluble<sup>(54)</sup> in ether at the following conditions: 3-5 grams per 100 grams at 25°C, 20-30 grams per 100 grams at the boiling

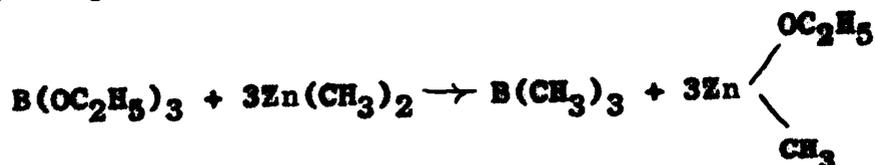
point of a saturated solution. Also, lithium borohydride was soluble in tetrahydrofuran, 28 grams per 100 grams at 25°C, and in amines.

Sodium Borohydride. Sodium borohydride, a white crystalline solid, was found to decompose in water and air. It was insoluble<sup>(55)</sup> in dioxane, ethyl ether, diethyl amine, and methyl borate, and soluble in pyridine 3.5 grams per 100 grams, ethylene diamine 22 grams per 100 grams, methyl amine 27.6 grams per 100 grams, ethyl amine 20.9 grams per 100 grams, n-propyl amine 9.7 grams per 100 grams, isopropyl amine 6.0 grams per 100 grams, n-butyl amine, 4.9 grams per 100 grams, and liquid ammonia, 104 grams per 100 grams.

### Organo Boron Compounds

In this section is contained information on the preparation and some of the properties of the organo-boron compounds expected to be formed in this study.

Boron Trialkyls. Boron trialkyls were obtained<sup>(38)</sup> from esters of boric acid or boron trichloride on zinc dialkyls, but better by the action of boron trifluoride on alkyl magnesium salts.



or



The reaction<sup>(69)</sup> of boron trichloride and zinc dimethyl formed trimethyl boron, methyl dichloro-boron, and dimethyl chloro-boron, respectively. The two latter compounds cannot be distilled.

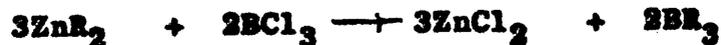
Properties of Boron Trialkyls. The boron trialkyls<sup>(24,38)</sup> were found to be colorless liquids, with a smell reminiscent of radishes and onions. They were oxidized on exposure to air, and were best handled under nitrogen. When oxidized, they burned with a green flame.

Boron trimethyl was a gas, and the triethyl, tripropyl, and tributyl boron compounds boiled at 95, 156, and 188°C, respectively.

Goubeau<sup>(28)</sup> in his review, listed preparations of boron trimethyl and triethyl from boron halides and the grignard reagent,



from boron halides and zinc alkyls,



and from boron halides and aluminum methyl.

Reaction of Diborane With Organic Compounds.

Diborane reacted<sup>(54)</sup> at 100°C with olefins by addition,

thus saturating the double bond and forming boron trialkyls.



Hurd<sup>(38)</sup> reported that by heating 1-butylene and 2-10 per cent diborane for 24 hours at 100°C, tertiary butyl boron  $(\text{C}_4\text{H}_9)_3\text{B}$ , boiling at 181.5°C, and isobutyl boron, boiling at 188.5°C were produced.

Ethylene and diborane heated for four days at 199°C formed triethyl boron.

Hurd<sup>(38)</sup> stated that the reaction of diborane with hydrocarbons was complex, involving paraffin chain breakdown and synthesis as well as the formation of boron-carbon bonds. It was possible that the active agent in addition and substitution reactions was borine,  $\text{BH}_3$ .

For physical properties of the organic derivatives of diborane see Table III, page 33.

#### Chemical Action of Boron Alkyls. Goubeau<sup>(28)</sup>

stated that boron methyl and ethyl react with amines forming colorless addition compounds, and listed many possible compounds that may be formed by the action of ammonia and various amines on boron alkyls.

Also, boron methyl and ethyl reacted with hydrogen halides in the molar ratio 1:1 at 150-180°C, in a closed tube, splitting off one mol of methane

TABLE III

Physical Properties of Organic Derivatives of Diborane<sup>a</sup>

Formula	Description	Process	Temperature °C
$(\text{CH}_3)_2\text{B}_2\text{H}_4$	Unsym. dimethyl diborane	fusion vaporization	-150.2 2.0
$(\text{CH}_3)_3\text{B}_2\text{H}_3$	1,1,2-trimethyl diborane	fusion vaporization	-122.9 45.0
$(\text{CH}_3)_4\text{B}_2\text{H}_2$	Sym. tetramethyl diborane	fusion vaporization	-72.5 72.0
$(\text{C}_2\text{H}_5)_2\text{B}_2\text{H}_4$	Unsym. diethyl diborane	vaporization	67.0
$(\text{C}_2\text{H}_5)_4\text{B}_2\text{H}_4$	Sym. tetraethyl diborane	fusion	-56.3

a. Slechter, S. H., E. M. Adams, and C. E. Jackson; Boron Hydrides and Related Compounds, p. 37, Cellery Chemical Company, 1951

or ethane and forming the monohalogen boron alkyl  $BR_2X$ .



The boron alkyls reacted<sup>(55)</sup> with diborane to form mixtures of monoborane, diborane, triborane, and tetramethyldiboranes.

Methyl diborane has been best formed from boron methyl and a large excess of diborane at 80°C.

### III. EXPERIMENTAL

The experimental portion of this investigation consists of the purpose of investigation, plan of experimentation, materials, apparatus, method of procedure, data and results, and sample calculations.

#### Purpose of Investigation

The purpose of this investigation was to study the electrolysis of diethyl ether solutions of lithium methyl, lithium ethyl, lithium butyl, or ethyl magnesium bromide in the presence of lithium borohydride.

#### Plan of Investigation

The investigation consists of a survey of the literature pertinent to the project, and experimental work.

Literature Review. A thorough study of the literature cited in Chemical Abstracts was made on the chemical and physical properties of the alkali alkyls, and of the possible organo-boron compounds that may be formed in the electrolysis of an alkali alkyl in the presence of an alkali borohydride. Also

a review of the literature concerning other electrolytic sources of free radicals was made.

Production of Alkali Alkyls. The alkali alkyls to be used in this investigation are limited to those of the metal lithium, because of the solubilities of these compounds in organic solvents. Lithium butyl was produced by reacting lithium metal with butyl halides in an inert solvent under nitrogen. After this technique was developed, lithium methyl and lithium ethyl were prepared.

Conductivity of Solutions of Lithium Alkyls. A study was made of the conductivity of lithium butyl, lithium ethyl, and lithium methyl in various solvents in which lithium borohydride may be soluble.

Solubility of Lithium Borohydride. The solubility of lithium borohydride was determined in various solvents in which it was feasible to work with lithium alkyls.

Ethyl Magnesium Bromide. A study was made of the chemical and physical properties of ethyl magnesium bromide. Also, the conductivity of this compound in diethyl ether was determined.

Electrolysis. The electrolysis of the lithium alkyls or ethyl magnesium bromide in the presence of lithium borohydride was performed with a mercury

cathode and a platinum or other inert anode in a compatible solvent. The products of such electrolysis were collected, purified, and identified.

### Materials

In this section are the materials which were used in the experimental work.

Alcohol, Methyl. Absolute, code No 1214, lot No J331J. Obtained from General Chemical Division, Allied Chemical and Dye Corporation, New York, New York. Used with dry ice as condensing agent for ether and to destroy excess sodium hydride.

Benzene. Purified, 99 to 100 per cent, code No 1444, lot No H086. Obtained from General Chemical Division, Allied Chemical and Dye Corporation, New York, New York. Used as solvent.

1-Bromobutane. Code No 51. Obtained from Eastman Organic Chemicals Distillation Products Industries, Rochester, New York. Used in preparation of lithium butyl.

Bromoethane. Ether-free, 500 grams, P-114. Obtained from Eastman Organic Chemicals Distillation Products Industries, Rochester, New York. Used in preparation of lithium ethyl.

Chlorobutane. Code No 52. Obtained from Eastman Organic Chemicals Distillation Products Industries, Rochester, New York. Used in preparation of lithium butyl.

Copper Wire. Gage No 18. Obtained from Blacksburg Hardware Company, Blacksburg, Virginia. Used for connections in electrolysis.

Drierite. Anhydrous calcium sulfate, size 6-mesh. Manufactured by W. A. Hammond Drierite Company, Xenia, Ohio. Used in drying tubes.

Ether, Ethyl. Code No 1699, Lot No J355J. Dry, code No 1706, lot No J083J. Specifications: Meets American Chemical Society standards, specific gravity 25/25°C, 0.712 to 0.714. Obtained from General Chemical Division, Allied Chemical and Dye Corporation, New York, New York. Used as solvent.

Glass Wool. Obtained from Fisher Scientific Company, Silver Spring, Maryland. Used as filtering agent.

Hydrochloric Acid. CP, catalog No A-144. Specifications: "Specific gravity, 1.1878 at 60°F, purity, not less than 37 per cent hydrochloric acid by volume." Obtained from Fisher Scientific Company, Silver Spring, Maryland. Used in analysis of lithium alkyls.

Ice, Dry. Solid carbon dioxide. Obtained from Clover Creamery, Radford, Virginia. Used in condenser and traps.

Iodomethane. Two hundred grams, code No 164. Obtained from Eastman Organic Chemicals Distillation Products Industries, Rochester, New York. Used in preparation of lithium methyl.

Lithium Borohydride. Prepared by R. S. Tinsley<sup>(80)</sup>. Used in electrolyses.

Lithium Chloride. CP, lot No 521892, catalog No L-121. Obtained from Fisher Scientific Company, Silver Spring, Maryland. Used in preparing lithium borohydride.

Lithium Metal. CP, code No L-111, control No 510420. Obtained from Fisher Scientific Company, Silver Spring, Maryland. Used to prepare lithium alkyls.

Lithium Metal. Wire, one-eighth inch diameter. Obtained from A. D. McKay, Inc., New York 38, New York. Used to prepare lithium alkyls.

Magnesium. Metal ribbon, code No 1901. Obtained from General Chemical Company, New York, New York. Used in preparing ethyl magnesium bromide.

2-Methylbutane. Practical, 1000 grams. Obtained from Eastman Organic Chemicals Distillation Products Industries, Rochester, New York. Used as solvent.

Mercury. Technical. Manufactured by Metal Salts Corporation, Hawthorne, New Jersey. Used as an atmospheric seal and as cathode material.

Mineral Oil. USP, heavy, white. Obtained from Tech Drug Store, Blacksburg, Virginia. Used as a storing medium for lithium metal.

Nitrogen. Oil pumped. Obtained from The Matheson Company, East Rutherford, New Jersey. Used as an inert atmosphere.

Petroleum Ether. CP, catalog No E-139. Analysis: "Appearance and color, clear and colorless; odor, passes test; boiling, range 32 to 57°C; free acid, none; fats and oils, none; non-volatile matter, 0.001 per cent." Obtained from Fisher Scientific Company, Silver Spring, Maryland. Used as solvent.

Phenolphthalein. USP, powder, code No 2051, lot No 23. Obtained from General Chemical Company, New York, New York. Used as indicator.

Platinum. Sheet, 0.001 inch thick. Obtained from J. Bishop and Company Platinum Works, Malvern, Pennsylvania. Used as anode in electrolysis.

Potassium Permanganate. Crystal, code No 2125, lot J119. Obtained from General Chemical Division, Allied Chemical and Dye Corporation, New York, New York. Used to test exit gases from electrolysis.

N-Propyl Amine. Code No 1216, boiling point 48 to 50°C. Obtained from Eastman Organic Chemicals Distillation

Products Industries, Rochester, New York. Used as solvent in preparing lithium borohydride.

Sodium Carbonate. Anhydrous powder, code No 2248, lot No HCO2. Meets American Chemical Society specifications. Obtained from General Chemical Division, Allied Chemical and Dye Corporation, New York, New York. Used as standard for hydrochloric acid solution.

Sodium Hydride. Lot No 921. Obtained from Metal Hydrides, Inc., Beverly, Massachusetts. Used to dry ether.

Sodium Hydroxide. Pellets, code No 7708, control No W3SX. Specifications: "Meets with American Chemical Society standards." Obtained from Mallinckredt Chemical Works, New York, New York. Used for analysis of grignard compound.

Sulfuric Acid. CP, code No 1180. Specifications: "Assay, 95.5 to 96.5 per cent; specific gravity, 1.84; maximum limits of impurities, non-volatile, 0.004 per cent; chloride, 0.00002 per cent; nitrate, 0.00002 per cent; ammonium, 0.0001 per cent; sulfur dioxide, 0.0003 per cent; arsenic, 0.0000005 per cent; iron, 0.00002 per cent; heavy metals, 0.00008 per cent." Obtained from General Chemical Division, Allied Chemical and Dye Corporation, New York, New York. Used in analysis.

Turmeric. Commercial grade. Obtained from The A. & P. Tea Company, Blacksburg, Virginia. Used in analysis.

Water, Distilled. Once distilled. Prepared from Virginia Polytechnic Institute well water. Used as solvent.

### Apparatus

In this section the apparatus used in the experimental work is listed.

Adapter. Ground-glass joint, 29/42, catalog No 1-034. Obtained from Fisher Scientific Company, Silver Spring, Maryland. Used in distillation of solvents.

Ammeter. Direct current, range: 0 to 3 amperes in 0.05-ampere divisions; 0 to 30 amperes in 0.5-ampere divisions, model 489, serial No 6528. Manufactured by Weston Electrical Instrument Corporation, Newark, New Jersey. Used to measure current used in electrolysis.

Balance, Analytical. Chainomatic, serial No 48223B, capacity 200 grams, sensitivity 0.0001 gram. Manufactured by Seederer-Kohlbusch, Inc., Jersey City, New Jersey. Used to weigh product samples for analyses.

Balance, Triplebeam. Capacity 610 grams, sensitivity 0.1 gram. Manufactured by Ohaus, Newark, New Jersey.

Obtained from Phipps and Bird, Inc., Richmond, Virginia. Used to weigh chemicals.

Buret. Standard, capacity 50 ml at 20°C. Obtained from Fisher Scientific Company, Silver Spring, Maryland. Used in analytical determinations.

Condenser. Liebig type, two ground-glass joints, 29/42, catalog No 7-723-5. Obtained from Fisher Scientific Company, Silver Spring, Maryland. Used in distilling solvents and as reflux condenser.

Conductivity Cell. Dip type, platinum electrodes, electrode area 16 sq cm, catalog No 9-382. Obtained from Fisher Scientific Company, Silver Spring, Maryland. Used in measuring conductivities.

Desiccator. Plain, sheibler type, catalog No 8-595, inside diameter 200 mm. Obtained from Fisher Scientific Company, Silver Spring, Maryland. Used to store sodium hydride.

Flask. Dewar type, catalog No 10-196, two-quart capacity. Obtained from Fisher Scientific Company, Silver Spring, Maryland. Used with dry ice and methanol to trap exit gases from electrolysis.

Flask. Two, three-neck, one-liter capacity, ground-glass joints 29/42. Obtained from Fisher Scientific Company, Silver Spring, Maryland. Used in electrolysis, distillation, and preparation of compounds.

Generator. Direct current. Shunt wound, serial No 725, 55 volts, 90 amperes, 1750 revolutions per minute, 5 kilowatt. Manufactured by The Hertner Electric Company, Cleveland, Ohio. Obtained from L. J. Land, Inc., New York, New York. Used as the direct current source for electrolysis.

Heater, Autemp. Variable temperature, 450 watts, 115 volts, catalog No 11-425. Obtained from Fisher Scientific Company, Silver Spring, Maryland. Used as all-purpose heater.

Ice Machines. Manufactured by Victor Products Corporation, Hagerstown, Maryland. Used to supply ice for cooling reactions.

Motor. Serial No 726, 220 volts, ac, 20 amperes, 8 horse power, 750 revolutions per minute, 3 phase, 60 cycles. Obtained from L. J. Land, Inc., New York, New York. Used to drive generator.

Oscilloscope. Cathode-ray. Type 274-A, serial No 2306, 115/230 volts, ac, 50 to 60 cycles, 50 watts. Manufactured by Allen B. Dumont Laboratories, Inc., Passaic, New Jersey. Used to measure conductivities.

Oven. Electric utility, model OV-8, serial No 8-270, 115 volts, ac, 5 amperes. Manufactured by Modern Electric Laboratory, Chicago, Illinois. Obtained from Scientific Glass Apparatus Company, Inc., Bloomfield, New Jersey. Used to dry apparatus.

Pipettor, Caulfield. Obtained from Fisher Scientific Company, Silver Spring, Maryland. Used to withdraw samples for analysis.

Powerstat. Type 116, 115 volts, ac, 50 to 60 cycles, output range 6 to 135 volts, 7.5 amperes. Manufactured by Superior Electric Company, Bristol, Connecticut. Used to regulate heaters.

Resistor. Variable, catalog No 4261, serial No 1003353. Manufactured by Leeds and Northrup Company, Philadelphia, Pennsylvania. Used in conjunction with the oscilloscope to measure conductivity.

Resistor. Decade, No 82821D, range 0 to 100,000 ohms. Manufactured by Central Scientific Company, Chicago, Illinois. Used in conjunction with the oscilloscope to measure conductivity.

Rheostat. No 8070-V1, DL 2240005, G138, maximum 250 volts, 25 ohms, 5.2 amperes, resistance 3.41 ohms, for field. Manufactured by General Electric, Schenectady, New York. Used to control direct current generator.

Stirrer. Magnetic, 115 volts, ac, 50 to 60 cycles. Obtained from Fisher Scientific Company, Silver Spring, Maryland. Used to stir reaction mixture.

Thermometer. Ground-glass joint, mercury filled, range -10 to 360°C in 1° divisions. Obtained from Fisher Scientific Company, Silver Spring, Maryland. Used with ground-glass distillation apparatus.

Thermometer. Standard laboratory, mercury filled, catalog No 14-985, range -20 to 110°C in 1° divisions. Obtained from

Fisher Scientific Company, Silver Spring, Maryland. Used to measure reaction temperature.

Voltmeter. Direct current, ranges: 0 to 3 volts in 0.05-volt divisions, 0 to 7.5 volts in 0.1-volt divisions, 0 to 150 volts in 1.0-volt divisions, model No 489. Manufactured by Weston Electrical Instrument Corporation, Newark, New Jersey. Used to measure potential in electrolysis.

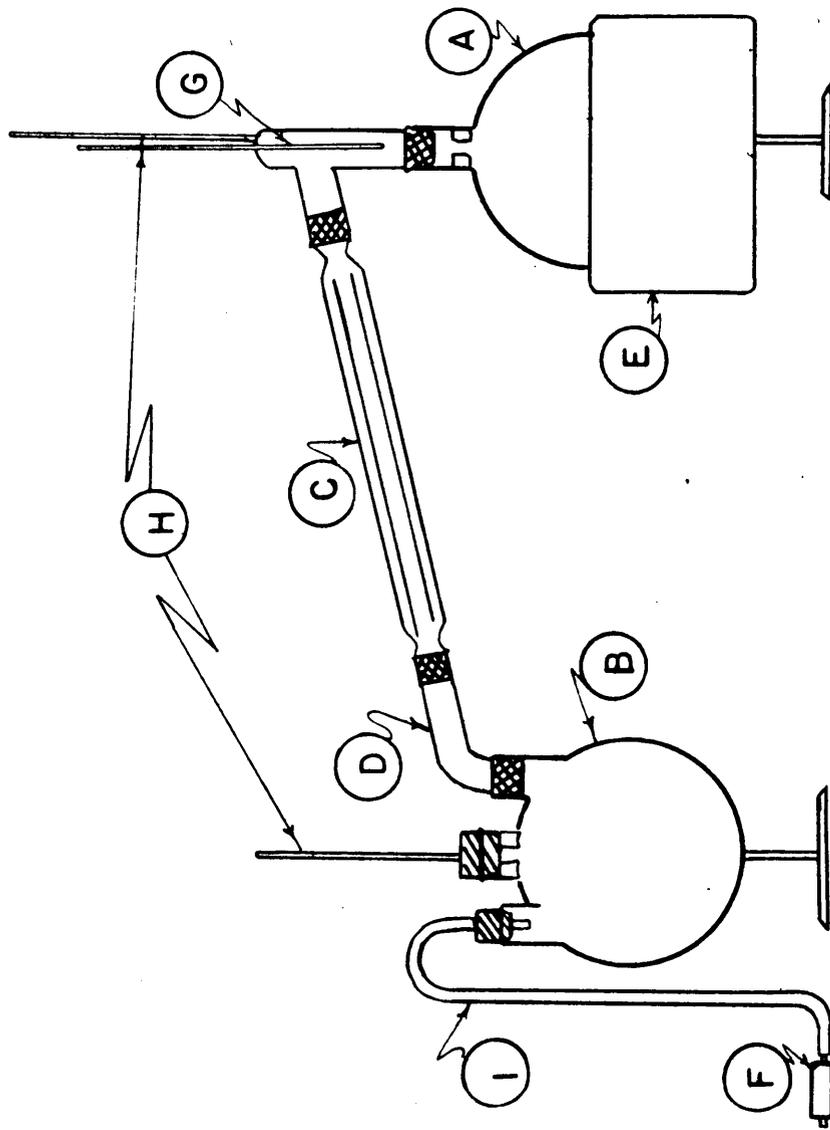
#### Method of Procedure

Drying Diethyl Ether. In drying the diethyl ether to be used as an inert solvent in the reaction of lithium metal with alkyl halides, to form the lithium alkyls, this general procedure was followed: To 2 liters of diethyl ether in a suitable container, containing approximately 0.5 per cent water, was added 10 grams of sodium hydride. The mixture was magnetically agitated for 24 hours, or until bubbles of hydrogen ceased to be evolved from the hydride. The container outlet was connected to a drying tube. To test the ether for dryness after 24 hours, a small amount of sodium hydride was added; if no bubbles evolved, the ether was assumed dry. This mixture was then poured into a one-liter, one-neck, round-bottom

distilling flask, and three-quarters of it distilled over the sodium hydride with a metal heating jacket, as shown in Figure 1, page 48. The ether was condensed into a three-neck flask, with the only outlet connected to a drying tube. The three-neck flask contained one-half gram of fresh sodium hydride. The distilling flask was allowed to cool, and the dried ether which had been condensed in the three-neck flask was poured into a two-gallon, screw-cap bottle for storage. Then the three-neck flask was replaced in the apparatus and more of the mixture to be distilled was added. This was continued until the desired amount of dry ether was obtained. Before using the ether from the storage bottle, it was poured into a one-liter flask containing sodium hydride, and sealed with a drying tube. The ether was then allowed to stand until gas ceased to be given off. Then it was carefully decanted from the flask when needed.

Drying Petroleum Ether and Benzene. In drying petroleum ether or benzene, approximately two liters of the solvents were added to two grams of sodium hydride and allowed to stand six to eight hours with magnetic agitation. The solvents were then distilled by the same procedure used for diethyl ether, with the exception that there was need for sodium hydride in

NOTE: EQUIPMENT CONTAINED IN HOOD WITH  
DUCT TO CARRY AWAY FUMES.



- A- DISTILLING FLASK
- B- RECEIVING FLASK
- C- CONDENSER
- D- ADAPTER
- E- HEATING JACKET
- F- DRYING TUBE
- G- THERMOMETER
- H- STANDS
- I- RUBBER TUBING

FIGURE 1. APPARATUS FOR DISTILLING DRIED SOLVENT

the three-neck receiving flask. The solvents were then stored for later use.

Standardization of Hydrochloric Acid. The hydrochloric acid to be used in analysis was carefully standardized by titrating against sodium carbonate. A sample of dried sodium carbonate was weighed to 0.1 milligram in a weighing bottle. The sample of sodium carbonate was then transferred to a 500-milliliter erlenmeyer flask and approximately 100-milliliters of water added. The solution was then placed on a hot plate and brought to a boil. The boiling solution was then titrated, with the flask on the hot plate, with the hydrochloric acid. Phenolphthalein was used as an indicator.

Preparation of Lithium Metal. The lithium metal used in the reaction with alkyl halides was prepared in one of three ways. The first method was as follows: lithium chunks were weighed, then hammered thin in a copper dish under mineral oil. The flattened strips were cut with heavy shears into small pieces and dropped directly into the reaction flask. In the second method, the chunks of lithium were weighed, and cut with heavy scissors into the reaction flask, without hammering. The third method of preparation was by determining the weight per inch length of

lithium wire, measuring the desired length of lithium, cutting the one-eighth inch diameter wire into approximately one-half inch lengths and dropping them directly into the reaction flask.

Preparation of Lithium Butyl in Petroleum Ether.

In preparing lithium butyl in petroleum ether, 1.5 to 3.0 grams of lithium metal, prepared by any one of the three methods mentioned previously, were weighed, and cut directly into a one-liter, three-neck, round-bottom flask, equipped with a nitrogen sweep, a condenser, a magnetic stirrer, a dropping funnel, a thermometer, and drying tubes on the nitrogen outlet and inlet, as shown in Figure 2, page 51. To the flask were added from 25 to 50 milliliters of petroleum ether. The nitrogen was then cut off with a screw clamp and 10 to 10.5 milliliters of butyl bromide or chloride added through the dropping funnel. The reaction was characterized by a purplish color appearing on the surface of the lithium and in the body of the solution, and a rise in temperature of the mixture. The reaction was allowed to continue until the temperature in the flask returned to the starting temperature. At the end of the reaction, 200 milliliters of petroleum ether were added to the cooled flask.

- A - REACTION FLASK
- B - DROPPING FUNNEL
- C - MAGNETIC STIRRER
- D - SCREW CLAMP
- E - NITROGEN INLET
- F - DRYING TUBE
- G - REFLUX CONDENSER

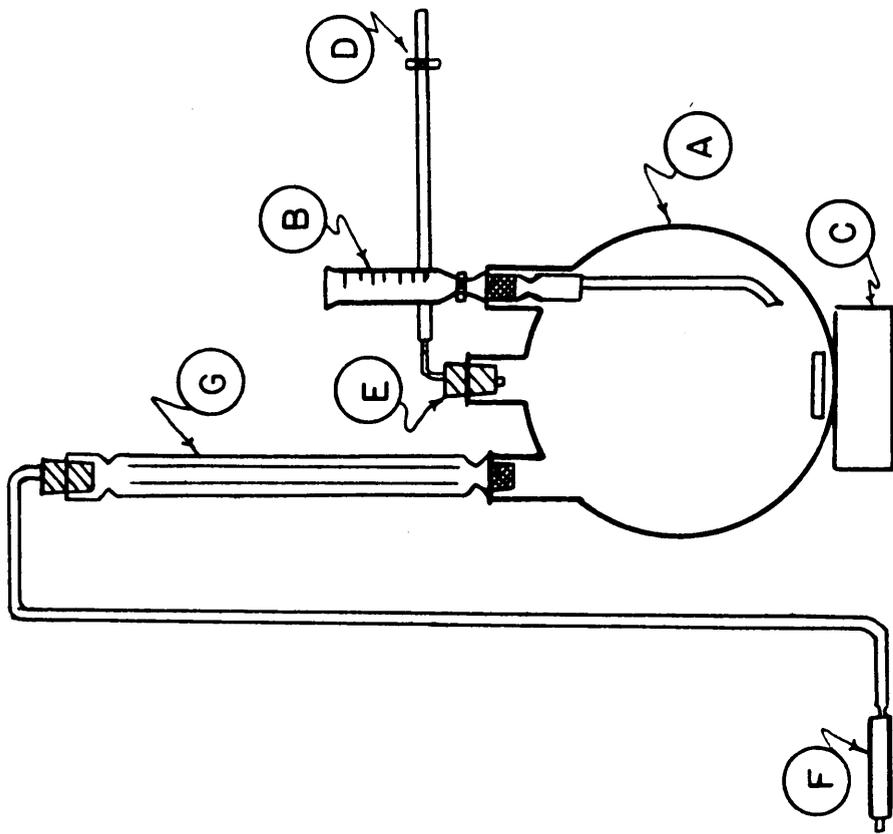


FIGURE 2. APPARATUS FOR PREPARATION OF  
LITHIUM ALKYLs

Preparation of Lithium Butyl in Benzene. An

attempt to prepare lithium butyl in benzene was made by reacting 3.0 grams of lithium metal with 10 milliliters of butyl bromide in 150 milliliters of dry benzene. The procedure was the same as for the preparation in petroleum ether.

Decanting and Filtering Lithium Butyl Solution.

The solution was decanted from the unreacted lithium and lithium halide by inserting the glass tube "F" in Figure 3, page 53, almost to the level of the solids in the flask. The screw clamp "B" was then slowly opened, allowing nitrogen pressure to force the liquid up the tube through the glass wool filter, and into the weighed flask, "I".

Analysis of Lithium Butyl. The receiving flask "I", in Figure 3, page 53, containing the filtered solution of lithium butyl in petroleum ether was weighed again to determine the weight of the solution. Then a 10-milliliter portion of the solution was withdrawn using a 10-milliliter pipet equipped with a pipettor. The sample was weighed in a tared, ground glass stoppered, weighing bottle. Then the sample was poured into a 250-milliliter erlenmeyer flask and 20 milliliters of water were added. The mixture was allowed to stand one minute. A drop of phenolphthalein

- A — REACTION FLASK
- B — SCREW CLAMP
- C — NITROGEN INLET
- D — SOLUTION
- E — SOLIDS
- F — GLASS TUBING
- G — FILTER
- H — GLASS WOOL
- I — RECEIVING FLASK
- J — DRYING TUBE
- K — STANDS

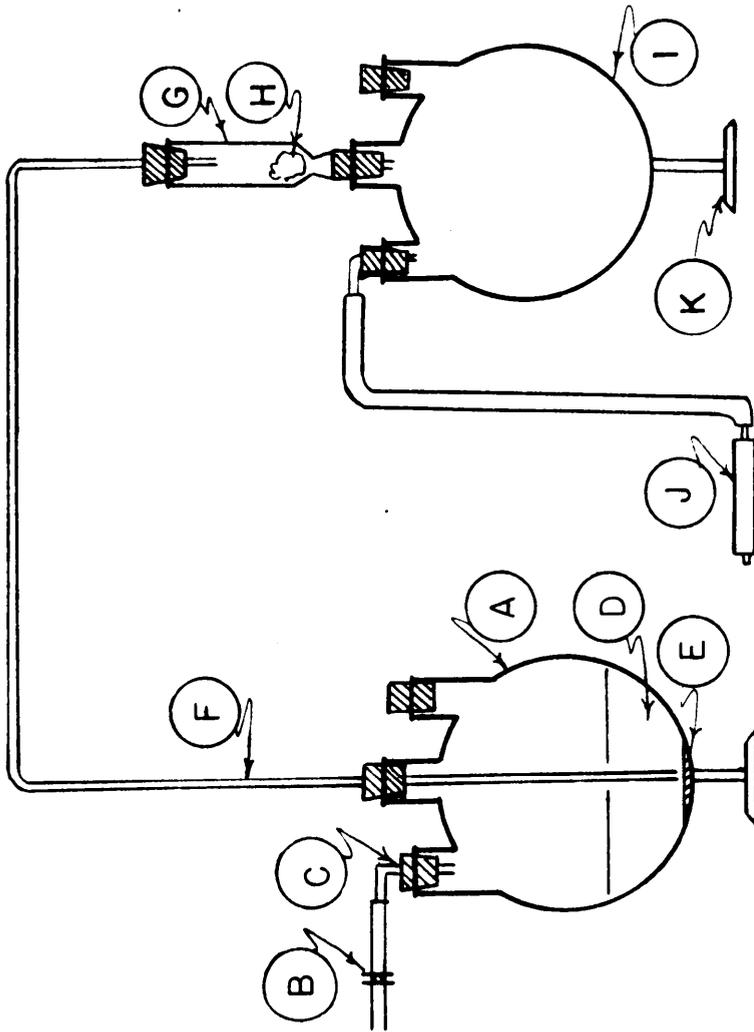


FIGURE 3. APPARATUS FOR DECANTING AND FILTERING  
LITHIUM ALKYL SOLUTIONS

was then added and the water layer was titrated with standard hydrochloric acid.

Transfer of Lithium Butyl to Diethyl Ether. The solution containing the lithium butyl was decanted into a one-liter, single-neck, round-bottom distilling flask, shown in Figure 4, page 55, which had been purged with nitrogen. All but approximately 20 milliliters of the petroleum ether were distilled off and then 100 milliliters of diethyl ether were added. Distillation was continued until approximately 20 milliliters of solution remained in the flask. Then the flask was allowed to cool, and 200 milliliters of diethyl ether were added. This solution was then transferred to a clean one-liter, three-neck, round-bottom flask, and stoppered.

Determination of the Resistance of the Lithium Butyl-Ether Solution. In determining the resistance of the lithium butyl solution, a standardized conductivity cell was carefully lowered into 50 milliliters of lithium butyl. The leads from the cell were then connected into a circuit for determining the resistance of the cell. The oscillator "A" and the oscilloscope, shown in Figure 5, page 56, were then turned on. The vertical amplitude on the oscilloscope "E" was adjusted to a convenient length, and the slide wire "D" set

- A- DISTILLING FLASK
- B- SCREW CLAMP
- C- NITROGEN INLET
- D- GROUND GLASS STOPPER
- E- HEATING JACKET
- F- THERMOMETER
- G- CONDENSER
- H- RECEIVING FLASK
- I- DRYING TUBE
- J- STANDS
- K- RUBBER TUBING

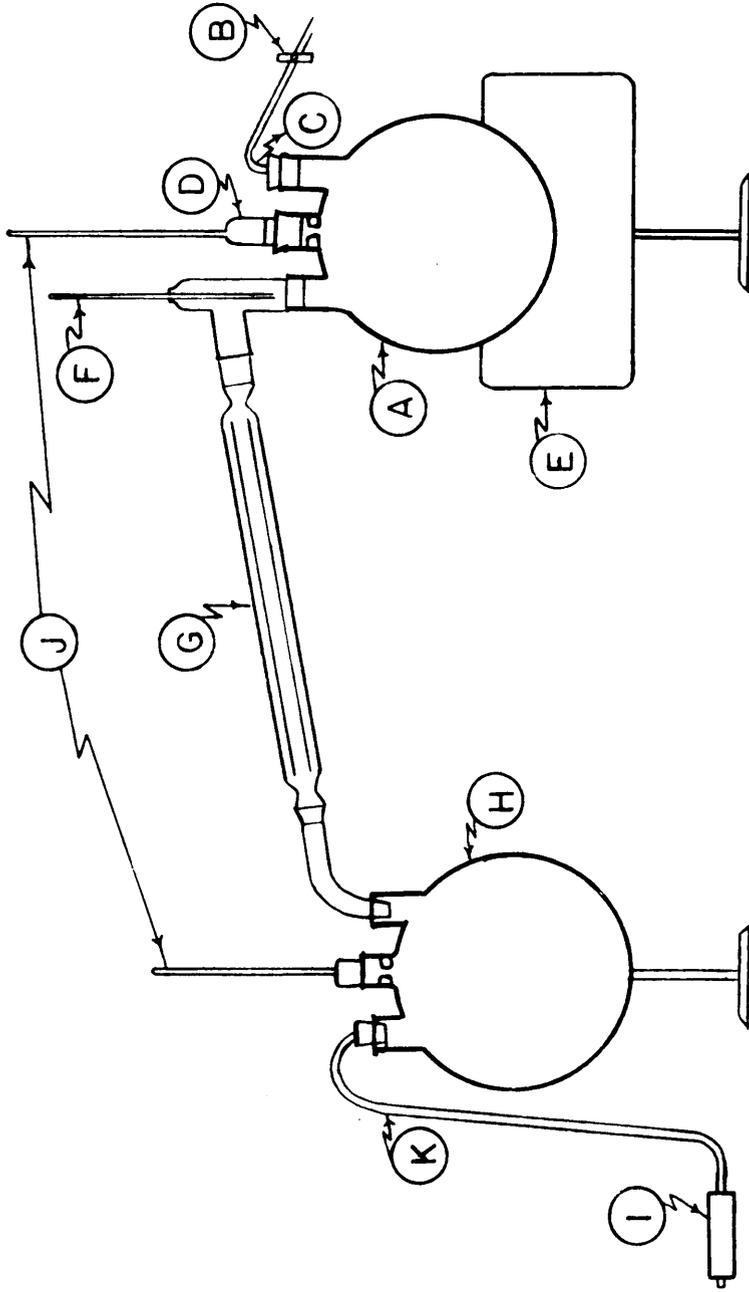
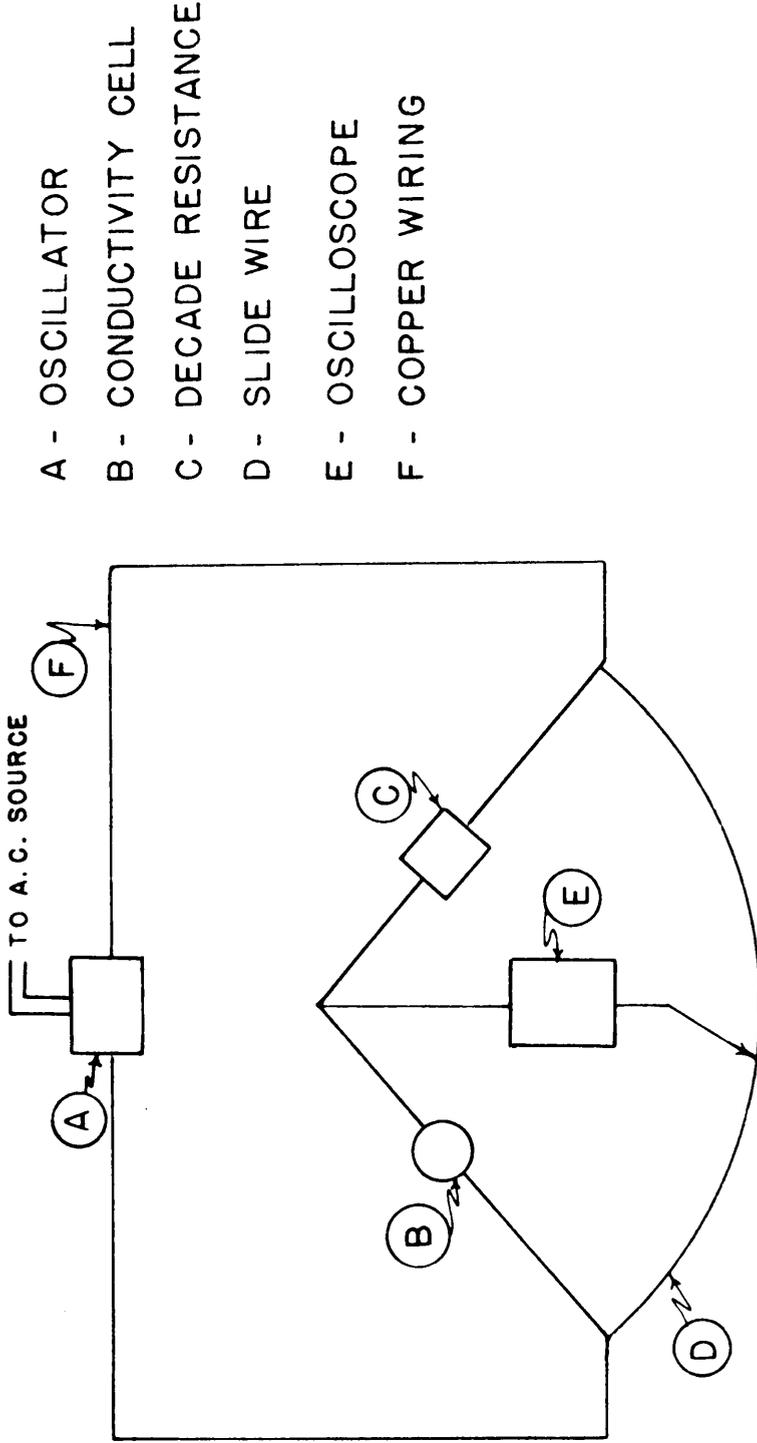


FIGURE 4. APPARATUS FOR TRANSFERRING LITHIUM ALKYLs FROM ONE SOLVENT TO ANOTHER



A - OSCILLATOR

B - CONDUCTIVITY CELL

C - DECADE RESISTANCE

D - SLIDE WIRE

E - OSCILLOSCOPE

F - COPPER WIRING

FIGURE 5. APPARATUS FOR CONDUCTIVITY DETERMINATION

on 500. The resistance in the resistance box "C" was increased until the vertical line on the oscilloscope "E" passed through a minimum. Then the slide wire was adjusted carefully to find the exact point of minimum. When this was found, the box reading and the slide wire reading were recorded. Then 0.13 gram of lithium borohydride was added to the solution, and the conductivity again determined.

Preparation of Lithium Methyl. Lithium methyl was prepared from the reaction of one to four grams of lithium metal in the form of cut blocks or cut wire and eight to nine milliliters of methyl iodide. The procedure and apparatus were the same as those for lithium butyl except that the reaction would not take place in petroleum ether. The metal was cut directly into a one-liter, three-neck flask in the same equipment used for preparing lithium butyl. The reaction was allowed to continue until the temperature of the mass fell 10 or more degrees centigrade.

Salting Out Lithium Iodide. The ether solution was filtered and decanted by the procedure given on page 52, and the solution transferred to a one-liter, single-neck, round-bottom distilling flask, see Figure 4, page 55. The diethyl ether was distilled off until only 15 to 25 milliliters remained in the

flask. Then 100 to 150 milliliters of petroleum ether were added and this distilled until only 20 milliliters of the liquid was left. Then the flask was cooled and 200 milliliters of petroleum ether added. This solution was then separated from the lithium iodide by decanting and filtering by the procedure given on page 52.

Determination of Conductivity of Lithium Methyl in Diethyl Ether. The purified solution of lithium methyl in petroleum ether was then transferred back into solution in diethyl ether by distilling off the petroleum ether and adding 200 milliliters of diethyl ether as in the above procedure. Then the conductivity before and after addition of 0.12 gram of lithium borohydride was determined by the procedure given on page 54.

Determination of Cell Constant. The constant for the cell used in the determination of the conductances was obtained by preparing a 0.1 normal solution of potassium chloride and measuring its resistance. Knowing the specific conductance of potassium chloride at a given temperature, the cell constant could be obtained from the data. The solution of potassium chloride was prepared by weighing 1.8638 grams of the crystal and making up

250 milliliters of solution in water. The temperature of this solution was adjusted to 25°C by immersion, for four hours, in a constant temperature bath. The cell resistance was then determined by the procedure given on page 54.

Preparation of Lithium Ethyl in Petroleum Ether.

Lithium ethyl was first prepared from 1.2 grams of lithium metal, in the form of cut blocks or wire, and 15 milliliters of ethyl bromide in 25 milliliters of petroleum ether. The procedure and apparatus used was the same as that for lithium butyl and lithium methyl. Also, in some instances, 25 milliliters of diethyl ether were used as the solvent rather than petroleum ether.

A second method of preparation<sup>(61,62)</sup> was employed using isopentane as the solvent. In this case, 3.8 grams of lithium in the form of wire were added to 200 milliliters of isopentane. Then 17.5 milliliters of ethyl bromide were slowly added through the dropping funnel "B". The apparatus was the same as that used in the preparation of the other lithium alkyls and is shown in Figure 2, page 51.

Transfer of Lithium Ethyl From Isopentane to Diethyl Ether. The solution of lithium ethyl in isopentane was decanted, and filtered as described

on page 52, using the apparatus shown in Figure 3, page 53. The solution was filtered into a one-liter, round-bottom distilling flask. Then the isopentane was distilled off, using the apparatus shown in Figure 3, page 53, until only 20 to 25 milliliters of solution remained in the bottom of the distilling flask. The flask was allowed to cool and 100 milliliters of diethyl ether added. This was then distilled off until about 10 to 20 milliliters of the original solution remained. Then the flask was cooled again and 200 milliliters of diethyl ether added.

Determination of Conductance of Ethyl Lithium in Diethyl Ether. The conductance of ethyl lithium was determined employing the procedure described on page 54. The apparatus used is shown in Figure 5, page 56. The resistance of the solution was measured before and after adding 0.11 gram of lithium borohydride.

Preparation of Ethyl Magnesium Bromide. With heavy scissors, 4.1 grams of magnesium strips were cut, and weighed in a tared, ground glass stoppered weighing bottle. This was added to 100 milliliters of diethyl ether contained in flask "A" shown in Figure 2, page 51. Then 13 milliliters of ethyl

bromide were slowly added to the flask from dropping funnel "B". The reaction was allowed to proceed for 1.5 hours and then the ether solution of the grignard compound was decanted and filtered, by the procedure given on page 52.

Analysis of Grignard Solution. To determine the amount of grignard compound present, a 10 milliliter aliquot portion of the solution in ether was withdrawn from the flask "I" in Figure 3, page 53, using a pipet equipped with a pipettor. The solution was transferred to a tared ground glass stoppered weighing bottle, weighed, and then slowly poured into a 500 milliliter erlenmeyer flask containing 50 milliliters of water. The weighing bottle was washed with a few milliliters of 0.193 normal sulfuric acid, and the washings added to the flask. Then an excess of sulfuric acid was added to the solution in the flask. The mixture was heated on a hot plate and boiled one to two minutes. The flask was cooled and the excess sulfuric acid back titrated, using standard sodium hydroxide with methyl orange as an indicator.

Removal of Unreacted Ethyl Bromide. The ether solution of ethyl magnesium bromide was transferred to a one liter, three neck flask as shown in Figure 4, page 55. The mixture was distilled until

about 10 to 20 milliliters of the original liquid remained in the flask. It was assumed that the ethyl bromide would be removed from the solution by this procedure. After the flask had been cooled, 200 milliliters of dry ether were added.

Conductivity Determination of Ethyl Magnesium Bromide in Diethyl Ether. The conductivity of the ether solution of the grignard compound was determined by the procedure given on page 54. The apparatus used is shown in Figure 5, page 56.

Conductivity of Solution of Grignard Compound and Lithium Borohydride. A solution of four tenths gram of lithium borohydride in 50 milliliters of diethyl ether was added to the flask containing the grignard compound from a dropping funnel with glass wool in the bottom to filter out any undissolved borohydride. The mixture was agitated to mix the solutions and then the conductivity was determined by the procedure given previously.

Electrolysis of Lithium Borohydride and Ethyl Magnesium Bromide in Diethyl Ether. For the electrolysis, the grignard solution was prepared as described before, analyzed, decanted, and filtered into the flask, shown in Figure 6, page 63. A weighed amount of lithium borohydride was dissolved in ether

A- GAS WASHING  
BOTTLE

B- TRAPS

C- PLATINUM  
ANODE

D- MERCURY  
CATHODE

E- MAGNETIC  
STIRRER

F- AMMETER

G- VOLTME-  
TER

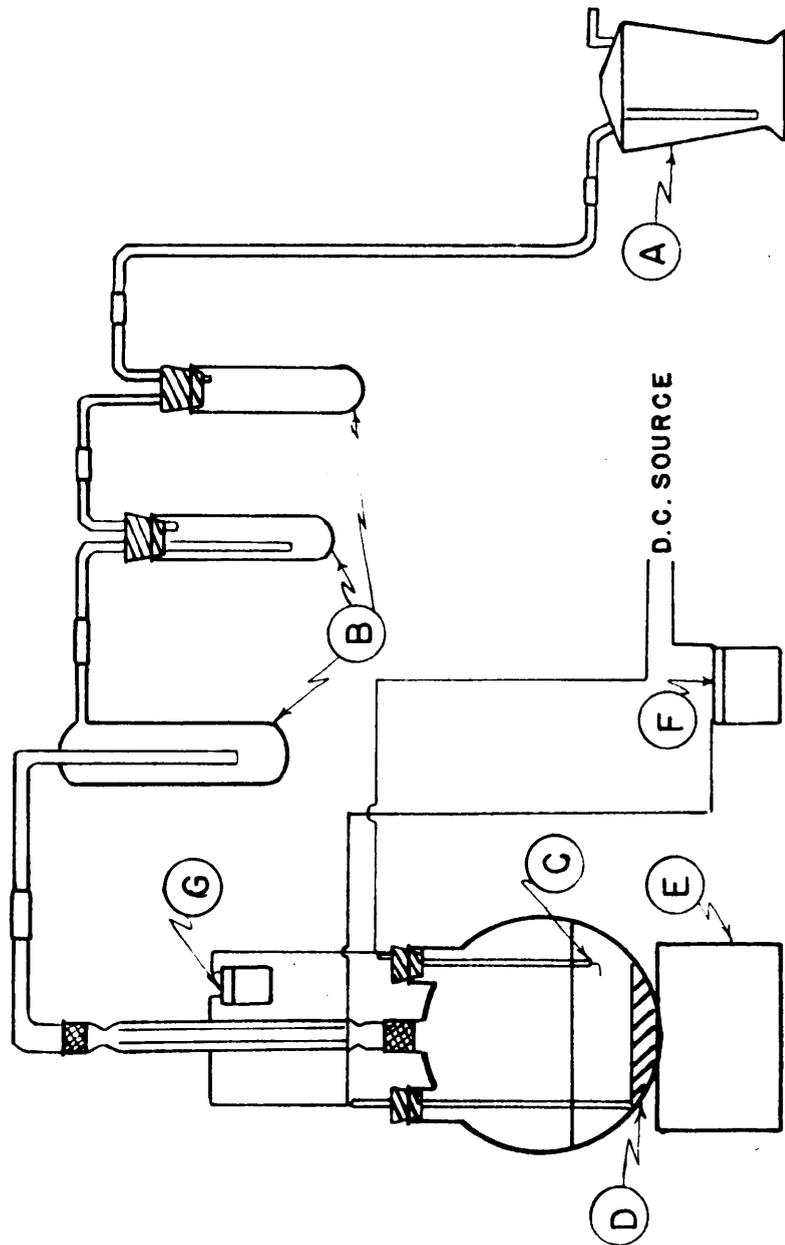


FIGURE 6. APPARATUS FOR THE ELECTROLYSIS OF  
ETHYL MAGNESIUM BROMIDE AND LITHIUM  
BOROHYDRIDE

and filtered through glass wool into the flask containing the grignard solution. The solution was magnetically agitated and the voltage was adjusted to 90 volts, giving a current of 0.075 ampere. Nitrogen was swept slowly through the system. The gases leaving the electrolysis flask were passed through one ice-water trap, the two dry-ice methanol traps, and then through a gas washing bottle containing 300 milliliters of a 0.075 normal solution of potassium permanganate.

Analysis of the Gases Evolved During Electrolysis.

A 10-milliliter sample from the permanganate solution in the gas washing bottle was titrated with standard sodium oxalate before and after the electrolysis. The cooling baths were removed from the traps and any vapors evolved were swept through the gas washing bottle. The permanganate solution was titrated as before with sodium oxalate. The liquid was tested with a saturated solution of turmeric in alcohol for boron content and its boiling point determined. By these tests it was ascertained that the liquid in the traps was ether, carried over from the electrolysis flask.

Second Electrolysis of Lithium Borohydride and Ethyl Mangesium Bromide in Ether. For the second

electrolysis, the constituents were the same as in the first electrolysis. However, instead of the ice traps and the permanganate solution, the gas washing bottle on the gas exit line was filled with water to hydrolyze any boron gases to borate ions. Also, a thimble condenser filled with dry ice-methanol mixture was added to condense the ether vapors. The apparatus is shown in Figure 7, page 66. The time of electrolysis was increased to 14 hours, and the voltage maintained at 93 volts.

#### Analysis of Gases Evolved During Electrolysis.

At the end of the electrolysis a sample of the water from the gas washing bottle was tested with a saturated solution of turmeric in ethyl alcohol. In the presence of the borate ion the solution turns from light orange to purplish-brown.

#### Transfer of Electrolysis Solution to Benzene.

The electrolyzed solution was transferred from ether to benzene to precipitate out the unreacted lithium borohydride. The transfer was made by distilling the ether from the electrolysis flask until approximately 20-30 milliliters of liquid remained, then 200 milliliters of benzene were added and this too distilled to approximately one fifth of its original volume. Then 200 more milliliters of benzene were added and the solution agitated.

- A - GAS WASHING BOTTLE
- B - TRAP
- C - MERCURY CATHODE
- D - PLATINUM ANODE
- E - THIMBLE CONDENSER
- F - ELECTROLYSIS FLASK
- G - MAGNETIC STIRRER

H - AMMETER

I - VOLTMETER

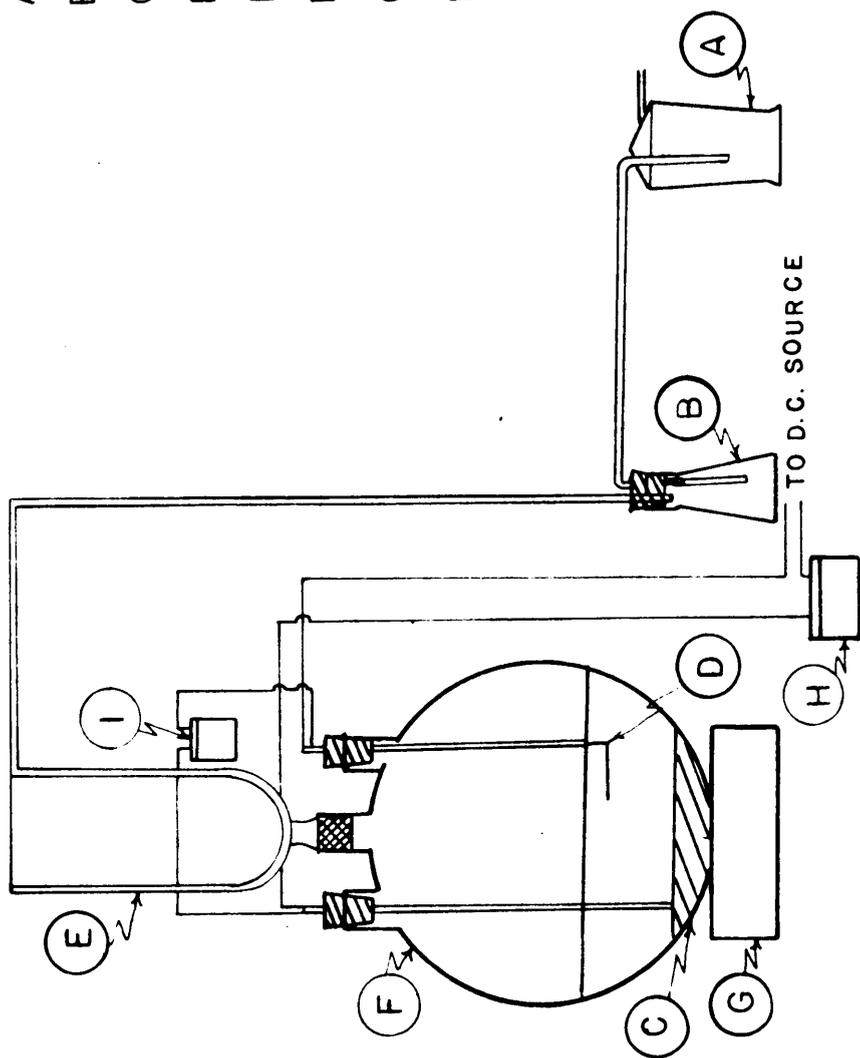
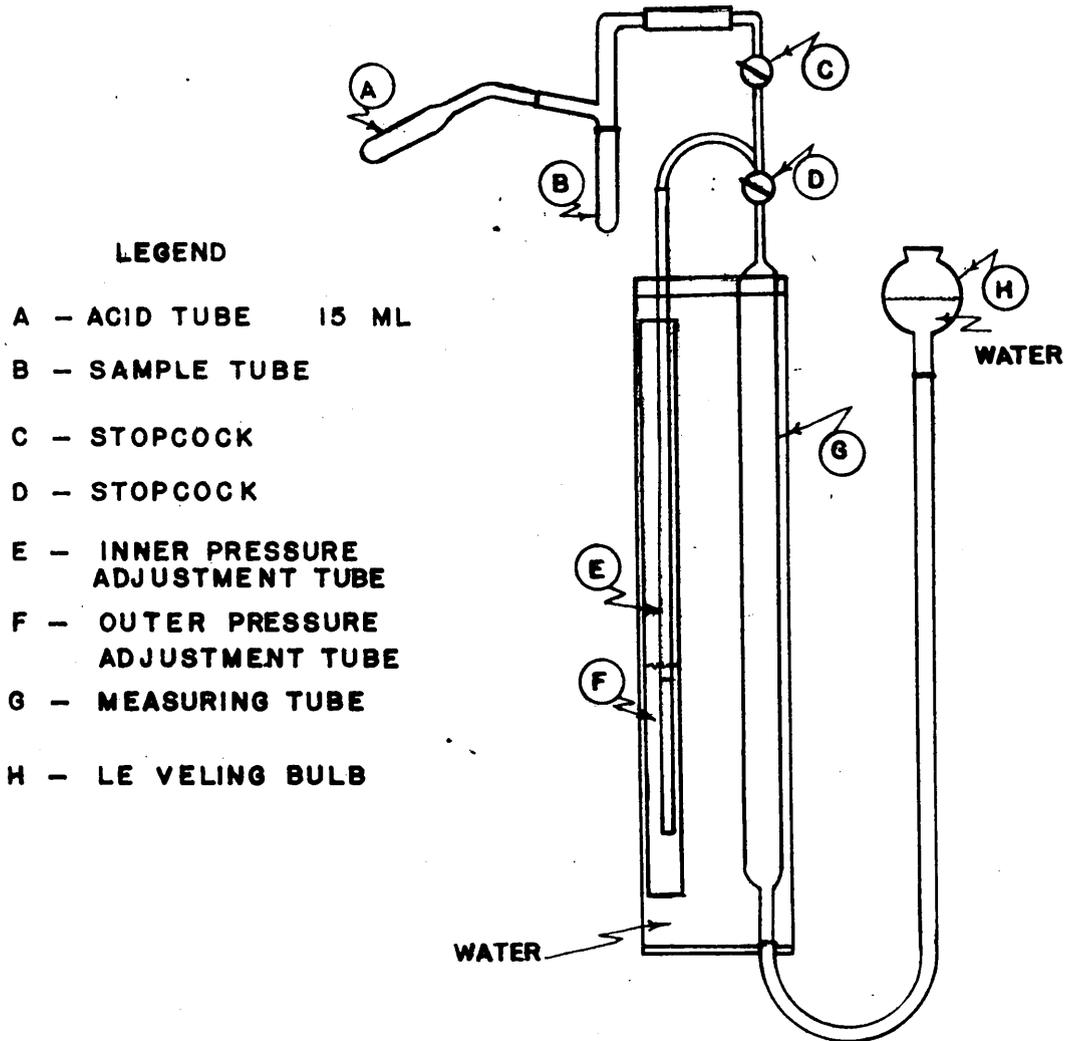


FIGURE 7. APPARATUS FOR THE ELECTROLYSIS OF  
ETHYL MAGNESIUM BROMIDE AND LITHIUM  
BOROHYDRIDE

Analysis of Benzene Solution. The electrolysis mixture now consisted of a clear benzene solution and a grey insoluble deposit on the mercury cathode. The benzene solution was analyzed for active hydrogen content and boron content.

Boron Analysis. The qualitative test for the presence of boron was to take the 10-milliliter sample to be tested and hydrolyze it with an equal amount of water. Then to this was added approximately 2-3 milliliters of a saturated solution of turmeric in ethanol.

Active Hydrogen Analysis. To determine the active hydrogen content in a sample the following procedure was employed, using the equipment shown in Figure 8, page 68. The sample tube "B" was weighed dry, then weighed again with the sample of the solution to be tested in it. Approximately 15 milliliters of acidified water were poured in the acid tube "A". The water level in tube "G" was adjusted to zero by raising the water bulb "H", with stopcock "C" open to the atmosphere. Then stopcock "C" was closed to the atmosphere and opened to the sample bottle with the water level in tube "G" at zero. Acid was carefully added to the sample by turning the acid tube "A". Then the sample was warmed until all evolution of gas ceased. The system was allowed to cool and then



**FIGURE 8. APPARATUS FOR DETERMINATION OF ACTIVE HYDROGEN**

stopcock "D" was opened to tube "E". The water bulb "H" was adjusted until the levels in tubes "E" and "F" were equalized. The water level in tube "G" was read as the volume of gas evolved. The atmospheric pressure and the temperature were recorded. The active hydrogen in the sample was calculated.

Transfer of Solution From Benzene Solvent to Ether Solvent. The benzene was then distilled from the electrolyzed solution in the electrolysis flask and ether added when all but 10-20 milliliters of benzene remained on the mercury in the flask. This was done to dissolve all of the precipitated lithium borohydride from the precipitate that was formed in the electrolysis.

Analysis of Ether Solution. A sample of grey deposit on the cathode was then agitated with ether, alcohol, and water and was found to be insoluble in each of these solvents. The material was then transferred to dilute hydrochloric acid, in which it dissolved within a minute, with evolution of gas. Then to the acid solution, concentrated sodium hydroxide was added and a white colloidal precipitate formed. A second sample of the material was transferred to a two per cent solution of silver nitrate to test for magnesium.

### Data and Results

The data and results obtained in the experimental section of this investigation are contained in the following section.

Preparation and Conductivities of Lithium Alkyls. The data and results obtained in the preparation of the lithium alkyls are shown in Table IV, page 71. The conductivities of the lithium alkyls in diethyl ether and in petroleum ether are contained in Table VI, page 73.

Conductivity Cell Constant. The data and results obtained in the determination of the conductivity cell constant are presented in Table V, page 72.

Preparation, Conductivity Determination, and Electrolysis of Ethyl Magnesium Bromide. The data obtained on the preparation of ethyl magnesium bromide are contained in Table VIII, page 75. The data and results obtained in the conductivity determination of solutions of ethyl magnesium bromide are given in Table VII, page 74, and in Table VI, page 73. The data and results obtained in the electrolysis of ethyl magnesium bromide in diethyl ether with lithium borohydride are given in Table IX, page 76, and Table X, page 77.

TABLE IV

Preparation of the Lithium Alkyls

Temperature of reaction, 35 °C  
 Normality of hydrochloric acid, 0.1323

Preparation number	Weight of lithium gm	Volume of halide ml	Method of preparing lithium	Time for reaction to start min	Time of reaction min	Volume of solvent ml	Weight of sample gm	Weight of solution in flask gm	Volume of hydrochloric acid ml	Yield %
1	3.00	10.5, C <sub>4</sub> H <sub>9</sub> Br	hammering	30.0	30.0	150 ml pet. ether	4.54	110.5	9.06	40.5
2	3.00	10.0, C <sub>4</sub> H <sub>9</sub> Br	hammering	30.0	480.0	150 ml benzene	4.33	117.7	0.55	2.9
3	2.00	25.0, C <sub>4</sub> H <sub>9</sub> Cl	hammering	30.0	-	25 ml diet. ether	8.43	73.1	0.00	0.0
4	1.72	10.0, C <sub>4</sub> H <sub>9</sub> Cl	cutting	0.5	60.0	25 ml pet. ether	5.85	169.5	8.15	66.6
5	1.44	10.5, C <sub>4</sub> H <sub>9</sub> Cl	cutting	0.5	60.0	25 ml pet. ether	3.08	178.0	5.15	80.5
6	3.60	9.0, CH <sub>3</sub> I	cutting	-	-	25 ml pet. ether	2.72	126.2	0.55	3.2
7	1.23	8.6, CH <sub>3</sub> I	cutting	-	-	25 ml pet. ether	-	-	0.00	0.0
8	1.01	10.5, CH <sub>3</sub> I	cutting	1.0	30.0	25 ml diet. ether	1.83	143.0	2.20	43.1
9	0.80	8.5, CH <sub>3</sub> I	cutting	0.5	45.0	25 ml diet. ether	3.92	131.0	2.50	26.4
10	1.09	10.0, C <sub>2</sub> H <sub>5</sub> Br	cutting	0.5	30.0	25 ml diet. ether	2.29	153.0	0.20	1.8
11	1.21	15.0, C <sub>2</sub> H <sub>5</sub> Br	cutting	1.0	30.0	25 ml pet. ether	4.09	132.0	2.25	15.2
12	0.97	15.0, C <sub>2</sub> H <sub>5</sub> Br	cutting	10.0	30.0	25 ml pet. ether	3.10	120.0	1.75	17.6
13	0.99	15.0, C <sub>2</sub> H <sub>5</sub> Br	wire	1.0	60.0	25 ml pet. ether	3.36	212.0	0.01	1.7
14	3.80	17.5, C <sub>2</sub> H <sub>5</sub> Br	wire	30.0	180.0	200 ml isopentane	2.91	169.0	0.40	18.4
15	3.00	10.0, CH <sub>3</sub> I	wire	0.5	60.0	25 ml diet. ether	2.99	129.0	5.00	24.4
16	3.80	17.5, C <sub>2</sub> H <sub>5</sub> Br	wire	30.0	240.0	200 ml isopentane	1.61	199.0	1.70	16.2
17	3.00	10.0, CH <sub>3</sub> I	wire	0.5	60.0	25 ml diet. ether	2.64	195.0	2.70	22.6

TABLE V

Determination of Conductivity Cell Constant

Weight of potassium chloride, gm	1.8634
Volume of water, ml	250.0
Temperature, °C	25.0
Concentration, normal	0.1
Resistance box, ohms	10.0
Slide wire	530.0
Specific conductance of 0.1 normal potassium chloride at 25° C, $\text{ohm}^{-1}\text{cm}^{-1}$	0.012886 <sup>a</sup>
Cell constant, $\text{cm}^{-1}$	0.1448

- a. Kortum, G. and J. O'M. Bockris: "Textbook of Electrochemistry",  
p. 13, Elsevier Publishing Co., New York, N. Y. 1951

TABLE VI

Conductivity of Solutions of Lithium Alkyls, Ethyl  
Magnesium Bromide, and Lithium Borohydride in Diethyl  
Ether and Petroleum Ether

Solvent	Solute	Resistance box ohms	Slide wire	Resistance ohms	Conductivity $\text{ohm}^{-1}\text{cm}^{-1}$	Molar conductance sq cm/ohm mol
50 ml petroleum ether	-	100,000	1000	$>10^8$	$<1.14 \times 10^{-9}$	- (a)
50 ml diethyl ether	-	100,000	1000	$>10^8$	$<1.14 \times 10^{-9}$	-
200 ml petroleum ether	2 gm lithium butyl	100,000	1000	$>10^8$	$<1.14 \times 10^{-9}$	-
200 ml petroleum ether	0.97 gm lithium methyl	100,000	1000	$>10^8$	$<1.14 \times 10^{-9}$	-
200 ml diethyl ether	1.1 gm lithium ethyl	100,000	920	$1.14 \times 10^6$	$1.26 \times 10^{-7}$	-
200 ml diethyl ether	1.1 gm lithium ethyl and 0.11 gm lithium borohydride (b)	100,000	915	$9.7 \times 10^5$	$1.5 \times 10^{-7}$	-
200 ml diethyl ether	0.91 gm lithium methyl	100,000	900	$9.0 \times 10^5$	$1.61 \times 10^{-7}$	-
200 ml diethyl ether	0.91 gm lithium methyl and 0.12 gm lithium borohydride (b)	100,000	905	$9.5 \times 10^5$	$1.55 \times 10^{-7}$	-
200 ml diethyl ether	2.75 gm lithium butyl	100,000	990	$9.9 \times 10^6$	$1.46 \times 10^{-8}$	-
200 ml diethyl ether	2.75 gm lithium butyl and 0.12 gm lithium borohydride (b)	100,000	990	$9.9 \times 10^6$	$1.46 \times 10^{-8}$	-
200 ml diethyl ether	13.3 gm ethyl magnesium bromide	7,000	415	$4.76 \times 10^3$	$3.98 \times 10^{-5}$	$6.16 \times 10^{-2}$
200 ml diethyl ether	13.3 gm ethyl magnesium bromide and 0.21 gm lithium borohydride (b)	30,000	405	$2.95 \times 10^4$	$0.7 \times 10^{-5}$	-
50 ml diethyl ether	0.04 gm lithium borohydride (b)	70,000	500	$7.0 \times 10^4$	$2.97 \times 10^{-6}$	$5.62 \times 10^{-2}$

a. Molar conductance was not calculated for those solutions where the conductivity of the solvent was an appreciable proportion of the total conductivity.

b. Lithium borohydride was added to the ether solutions as a solid, not as an ether solution.

TABLE VII

Effect of the Addition of Lithium Borohydride in  
Diethyl Ether on the Conductivity of Ethyl Magnesium  
Bromide in Diethyl Ether

Concentration of lithium borohydride in ether, molar	0.35
Volume of lithium borohydride solution added, ml	50.0
Concentration of ethyl magnesium bromide in ether, molar	0.5
Volume of ethyl magnesium bromide solution, ml	200.0
Cell constant, $\text{cm}^{-1}$	0.1448
Conductivity of solution before adding solution of lithium borohydride, $\text{ohm}^{-1}\text{cm}^{-1}$	$3.08 \times 10^{-5}$
Conductivity of solution after adding solution of lithium borohydride, $\text{ohm}^{-1}\text{cm}^{-1}$	$6.16 \times 10^{-5}$
Molar conductivity of ethyl magnesium bromide in diethyl ether, $\text{sg cm/ohm, mol}$	$6.16 \times 10^{-2}$
Conductivity of solution of lithium borohydride, ethyl magnesium bromide in ether, assuming additive properties, $\text{ohm}^{-1}\text{cm}^{-1}$	$3.35 \times 10^{-5}$

TABLE VIII

Yield Obtained in the Preparation of  
Ethyl Magnesium Bromide

Reagents:

Magnesium, 4.1 gm  
Diethyl ether, 100 ml  
Ethyl bromide, 13 ml

Preparation number	Weight of solution  gm	Sample weight  gm	Volume of 0.193 N. sulfuric acid  ml	Volume of 0.242 N. sodium hydroxide  ml	Yield  %
1	101.0	10.26	72.50	16.10	59.1
2	108.0	3.48	33.38	11.05	69.0
3	107.0	3.37	33.31	10.09	71.0
4	105.0	3.07	30.12	10.55	64.1

TABLE IX

Electrolysis of Ethyl Magnesium Bromide and Lithium

Borohydride in Diethyl Ether

Test number	1	2
Concentration of ethyl magnesium bromide, molar	0.366	0.392
Weight of solution, gm	307.0	315.0
Concentration of lithium borohydride, molar	0.375	0.365
Current, amperes	0.075	0.040 - 0.200
Potential, volts	90.0	93.0
Time of electrolysis, hours	3.0	14.0
Temperature, °C	35.0	35.0
Volume of mercury cathode, ml	100.0	100.0
Anode area, sq cm	6.45	6.45
Cathode area, sq cm	61.0	61.0
Cathode current density, amperes/sq dm	0.0012	0.0007 - 0.003
Anode current Density, amperes/sq dm	0.012	0.006 - 0.03
Observations		Gray material deposited at the cathode.

TABLE X

Analysis of Products of Electrolysis of Ethyl  
Magnesium Bromide and Lithium Borohydride in Ether

Barometric pressure, 710.18 mm of Hg  
Room temperature, 35 °C

Test number	1	2
<b>Reduction of potassium permanganate solution by exit gases</b>		
Volume of 0.0375 normal potassium permanganate, ml	10.00	a
Volume of 0.075 normal sodium oxalate for titration before electrolysis, ml	5.03	a
Volume of 0.075 normal sodium oxalate for titration after electrolysis, ml	4.94	a
<b>Hydrolysis of exit gases</b>		
Turmeric test	a	no color change, indicating no boron
<b>Benzene extraction of solution</b>		
Turmeric test	a	no color change, indicating no boron
Gas evolved when hydrolyzed, ml/gm	a	9.8
Weight of solution, gm	a	113.0
<b>Ether extraction of solution</b>		
Turmeric test	a	color change from orange to brown, indicating boron
Active hydrogen, milliatoms/gm	a	1.25
Weight of solution, gm	a	204.0
<b>Analysis of residue</b>		
Solubility	a	insol. in water, benzene, alcohol, and ether
Action with acids	a	reacts with dilute hydrochloric acid with evolution of gas
Neutralization of acid solution with sodium hydroxide	a	white precipitate forms when conc. sodium hydroxide is added
Action with 2 % silver nitrate solution	a	some blackening of surface, indicative of magnesium

a. data not determined

Sample Calculations

In this section are contained the sample calculations employed in this investigation.

Yield of Lithium Alkyl. The calculation for the yield of lithium alkyl from lithium metal in excess, and alkyl halide is shown below.

$$Y = \frac{(N_{\text{HCl}})(E)(V_{\text{HCl}})(W)(100)(M)}{(SW)(v_{\text{ah}})(d_{\text{ah}})(Li)}$$

where

- Y = yield of lithium alkyls, per cent
- $N_{\text{HCl}}$  = normality of hydrochloric acid, 0.1823
- E = equivalent weight of lithium per ml normal solution, 0.0069 gm
- $V_{\text{HCl}}$  = volume of hydrochloric acid, ml
- W = weight of solution, gm
- M = molecular weight of the lithium alkyl
- SW = sample weight, gm
- $v_{\text{ah}}$  = volume of alkyl halide used in reaction, ml
- Li = atomic weight of lithium
- $d_{\text{ah}}$  = density of alkyl halide, gm/ml

The data for this calculation are from Table IV, preparation No. 4, using butyl chloride (m. w. 137.03, density, 0.884 gm per ml).

$$Y = \frac{0.1823 \times .00694 \times 8.15 \times 169.5 \times 137.03 \times 100}{5.85 \times 10 \times 0.884 \times 6.94}$$

- 66.6%

The calculation for the yield of lithium alkyls when the alkyl halide is in excess is shown below.

$$Y = \frac{(N_{HCL})(E)(V_{HCL})(W)(2)(100)}{(W_{Li})(SW)}$$

where

Y = yield of lithium alkyl, per cent

E = equivalent weight of lithium per ml normal solution, 0.0069 gm

$N_{HCL}$  = normality of hydrochloric acid

$V_{HCL}$  = volume of hydrochloric acid, ml

W = weight of solution, gm

$W_{Li}$  = weight of lithium metal, gm

SW = sample weight, gm

The data for this calculation are from Table IV, preparation No. 8.

$$Y = \frac{0.1823 \times .00694 \times 2.20 \times 143.0 \times 2 \times 100}{1.83 \times 1.01}$$

= 43.1%

Concentration of Lithium Alkyl. The calculation for the concentration of lithium alkyls in ether is shown below.

$$C = \frac{V_{\text{HCL}} \times N_{\text{HCL}} \times W}{V_{\text{Et}} \times W_s}$$

where

C = concentration of lithium alkyl,  
mols/liter

$V_{\text{HCL}}$  = volume of hydrochloric acid, ml

$N_{\text{HCL}}$  = normality of hydrochloric acid

W = weight of solution, gm

$W_s$  = weight of sample, gm

$V_{\text{Et}}$  = volume of ether added, liters

The data for this calculation were taken from Table IV, page 71.

$$C = \frac{0.1823 \times 8.15 \times 169.5}{5.85 \times 1000 \times 0.2}$$

$$= 0.215 \text{ mols/liter}$$

Yield of Grignard Reagent. The calculation for the yield of ethyl magnesium bromide is shown below.

$$Y = \frac{(E) (V_{H_2SO_4} \times N_{H_2SO_4} - V_{NaOH} \times N_{NaOH}) (W) (100)}{W_{Mg} \times SW}$$

where

- Y - yield of ethyl magnesium bromide, per cent
- $V_{H_2SO_4}$  - volume of sulfuric acid, ml
- $N_{H_2SO_4}$  - normality of sulfuric acid
- $V_{NaOH}$  - volume of sodium hydroxide, ml
- $N_{NaOH}$  - normality of sodium hydroxide
- W - weight of solution, gm
- $W_{Mg}$  - weight of magnesium metal, gm
- SW - sample weight, gm
- E - equivalent weight of magnesium when magnesium hydroxy bromide is titrated by sulfuric acid, (0.02432)

The data for this calculation are from Table VIII, preparation No. 2.

$$Y = \frac{24.32 (33.38 \times 0.193 - 11.05 \times 0.242) (108) (100)}{4.1 \times 3.48}$$

- 69.0%

Concentration of Ethyl Magnesium Bromide. The calculation for the concentration of ethyl magnesium bromide in diethyl ether is presented below.

$$C = \frac{(V_{H_2SO_4} \times N_{H_2SO_4} - V_{NaOH} \times N_{NaOH})W}{V_{Et} \times W_s \times 1000}$$

where

C - concentration of ethyl magnesium bromide, mols/liter

$N_{H_2SO_4}$  - normality of sulfuric acid

$V_{H_2SO_4}$  - volume of sulfuric acid, ml

$V_{NaOH}$  - volume of sodium hydroxide, ml

$N_{NaOH}$  - normality of sodium hydroxide

W - weight of solution, gm

$W_s$  - sample weight, gm

$V_{Et}$  - volume of ether, liters

The data for this calculation were taken from Table VIII, page 75.

$$C = \frac{(72.5 \times 0.193 - 16.1 \times 0.242) 101}{10.26 \times 1000 \times 0.2}$$

- 0.498 mols/liter

Determination of Ethyl Magnesium Bromide. The calculation for the determination of the ethyl magnesium bromide content based on gas evolution, in the analytical determinations are shown below.

$$M_g = \frac{V_g (P_a - P_w) (T_s)}{W_s (22.4) (P_s) (T_a) (1000)} (W)$$

where

- Mg = amount of grignard reagent in sample, mols
- V<sub>g</sub> = volume of gas evolved, ml
- P<sub>a</sub> = actual barometric pressure, mm of Hg
- P<sub>w</sub> = vapor pressure of water, mm of Hg
- P<sub>s</sub> = barometric pressure at standard conditions, mm of Hg
- T<sub>s</sub> = temperature at standard conditions, °C
- T<sub>a</sub> = actual temperature, °C
- W<sub>s</sub> = sample weight, gm
- W = weight of solution, gm

The data for this calculation are from Table X, page 77.

$$M_g = \frac{4.8 (710.18 - 30.04) (273) (113)}{0.49 (22.4) (760) (300) (1000)}$$

= 0.040 mols

Resistance of Conductivity Cell. The calculation for the resistance in the cell from the box reading and the slide wire reading is shown below.

$$R = \frac{x (r)}{1000 - x}$$

where

R = resistance of solution, ohms

r = box reading, ohms

x = slide reading, ohms

The data for this calculation is shown in Table V, page 72.

$$R = \frac{530 (10)}{470} = 11.25 \text{ ohms}$$

Conductivity Cell Constant. The calculation for the cell constant for the standard cell used in measuring conductivities is shown below.

$$k = LR$$

where

k = cell constant,  $\text{cm}^{-1}$

L = specific conductance of a 0.1 N solution of potassium chloride at  $25^{\circ}\text{C}$ ,  $0.012886 \text{ ohm}^{-1}\text{cm}^{-1}$

R = resistance of solution, ohms

The data for this calculation is shown in Table V, page 72.

$$k = 0.012886 (11.25) = 0.1448 \text{ cm}^{-1}$$

Specific Conductance. The calculation for the specific conductance of a solution is shown below.

$$L = k/R$$

where

L = specific conductance,  $\text{ohm}^{-1}\text{cm}^{-1}$

R = resistance of solution, ohms

k = cell constant,  $\text{cm}^{-1}$

The data for this calculation is shown in Table VI, page 73.

$$L = 0.1448/9.9 \times 10^6$$

$$= 1.46 \times 10^{-8}$$

Molar Conductance. The calculation of the molar conductance of a solution from a knowledge of the specific conductance is shown below.

$$M = 1000 L/C$$

where

M = molar conductance,  $\text{cm}^2 \text{mol}^{-1} \text{ohm}^{-1}$

L = specific conductance,  $\text{ohm}^{-1} \text{cm}^{-1}$

C = concentration, mols/liter

The data for this calculation is from Table VII, page 74.

$$M = \frac{3.08 \times 10^{-5} \times 1000}{0.5}$$

$$= 6.16 \times 10^{-2} \text{ cm}^2 \text{ ohm}^{-1} \text{ cm}^{-1}$$

Conductance of Mixtures. The calculations for the molar conductance of a mixture, assuming colligative properties is shown below.

$$L = \frac{C_{Li} \times M_{Li} + C_{Et} \times M_{Et}}{1000}$$

where

- L = specific conductance of mixture,  $\text{ohm}^{-1} \text{cm}^{-1}$
- M = molar conductance of lithium borohydride,  $\text{cm}^2 \text{mol}^{-1} \text{ohm}^{-1}$
- $M_{Et}$  = molar conductance of ethyl magnesium bromide,  $\text{cm}^2 \text{mol}^{-1} \text{ohm}^{-1}$
- $C_{Li}$  = concentration of lithium borohydride, mols/liter
- $C_{Et}$  = concentration of ethyl magnesium bromide, mols/liter

The data for this calculation is from Table VII, page 74.

$$L = \frac{0.5 \times 6.16 \times 10^{-2} + 0.0485 \times 5.62 \times 10^{-2}}{1000}$$
$$= 3.35 \times 10^{-5} \text{ ohm}^{-1} \text{ cm}^{-1}$$

Current Density. The calculation for the current density at an electrode is shown below.

$$\text{C. D.} = \frac{\text{C} \times 100}{\text{A}}$$

where

C. D. = current density, amperes/dm<sup>2</sup>

C = current, amperes

A = electrode area, cm<sup>2</sup>

The data for this calculation is given in Table IX, page 76.

$$\begin{aligned} \text{C. D.} &= \frac{0.075 \times 100}{6.45} \\ &= 1.16 \text{ amperes/dm}^2 \end{aligned}$$

Determination of Active Hydrogen. The calculation for the active hydrogen content from the analytical determination, as outlined on page , is shown below. It was assumed that the vapor pressure of any solvent did not change the vapor pressure of water.

$$A_H = \frac{V_H (P_a - P_w)(T_s)}{W_s (22.4) (P_s) (T_a)}$$

where

- $A_H$  - active hydrogen content, milliatoms/gm
- $V_H$  - volume of hydrogen evolved, ml
- $W_s$  - weight of sample, gm
- $P_a$  - actual barometric pressure, mm of Hg
- $P_w$  - vapor pressure of water, mm of Hg
- $P_s$  - barometric pressure at standard conditions, mm of Hg
- $T_s$  - temperature at standard conditions, 273°K
- $T_a$  - actual temperature, °K

The data for this calculation were taken from Table X, page 77.

$$A_H = \frac{10.7 (710.18 - 30.04) (273)}{(0.3110) (22.4) (760) (300)}$$

= 1.25 milliatoms/gm

Lithium Borohydride Content. The calculation for the content of lithium borohydride in a solution based on the active hydrogen determination is shown below.

$$W_L = \frac{M_L \times W_s \times A_h}{N \times 1000}$$

where

$W_L$  - weight of lithium borohydride, gm

$W_s$  - weight of solution, gm

$M_L$  - molecular weight of lithium borohydride,  
21.79

$A_h$  - active hydrogen content, milliatoms/gm

$N$  - number of atoms of active hydrogen per mole  
of lithium borohydride, four.

The data for this calculation is from Table X,  
page 77.

$$W_L = \frac{21.79 \times 204 \times 1.25}{4 \times 1000}$$

- 1.38 gm

#### IV. DISCUSSION

The discussion is composed of a discussion of the results obtained in this investigation, the limitations imposed upon the investigation, and the recommendations for further study.

##### Discussion of Results

In the following section is contained a discussion of the results obtained in this investigation. The discussion covers the preparation of the lithium alkyls, the conductivities of the compounds studied in ether, and the electrolysis of ethyl magnesium bromide in diethyl ether.

Drying of Solvents. The simplest method for drying petroleum ether and benzene was to add approximately one gram of sodium hydride per 500 milliliters of solvent, allow the hydride to react and then to carefully decant the solvent. If the diethyl ether were dried in this manner, however, all of the sodium hydroxide formed would not settle out and a pure solvent could not be obtained without distillation.

Method of Preparing Lithium. The first method of preparing the lithium metal to be used was to hammer

the lithium out flat under an oil film and then to cut the lithium up into the reaction flask. The second method was to cut small slivers of lithium directly off a larger chunk of lithium into the flask. The reaction started much sooner when the lithium was prepared by the second method, than by the first, requiring approximately 30 seconds by the second method of preparation, and one half hour by the first. This is probably due to the fresh, bright surface offered when the lithium is freshly cut. In the hammering method, the lithium is excessively tarnished and the bright cut surface is small.

Preparation of Lithium Butyl. In preparing lithium butyl, the variables affecting the yield of product are the solvent that is used, the alkyl halide, reaction time, the method of preparing the lithium, the volume of solvent used and the ratios of reactants.

The three solvents used in preparing lithium butyl were petroleum ether, diethyl ether, and benzene. For the purposes of this investigation, solvents in which the by-product lithium halide is insoluble were preferred as these solvents provide a separation of the lithium alkyl and the lithium halide. The lithium halides are soluble in diethyl ether and

therefore, in general, the solvent used was petroleum ether, as the yield obtained in benzene was 2.9 per cent while the yields in petroleum ether were 40.5, 66.6, and 80.5 per cent. There was no yield of product obtained in diethyl ether but it is believed that a good yield could be obtained by adjusting the ratios of reactants. The molar ratios of butyl chloride to lithium was 0.82:1 in the preparation in diethyl ether, but for the reaction



the ratio of alkyl halide to lithium should be 0.5:1; therefore, the lithium alkyl formed when the ratio is higher than this is free to react with the excess halide,



completing the Wurtz reaction<sup>(20)</sup>. Also, when the ratio of petroleum ether to ethyl halide exceeds roughly 2.5:1, the yields began to decrease. For example, in run No. 5, the yield obtained at a ratio of solvent to halide of 2.5:1 was 80.5 per cent, while at a ratio of 5:1, the yield was 66.6 per cent and at 15:1 the yield was only 40.5 per cent.

In this investigation, it was found that the optimum time for reaction is approximately one hour. It is difficult to predict an exact optimum time on

the basis of the work done, as many factors were varied simultaneously, but in general, higher yields were found at reaction time of one hour than at one-half hour. Increasing the time above one hour does not result in any appreciable increase in yield as is evidenced by Run No. 2, which was carried on for eight hours with a yield of only 2.9 per cent.

The only instance in which the ratios of reactants had an appreciable effect on yield was when the preparation was performed in diethyl ether. In the preparations in petroleum ether, the molar ratio of lithium metal to alkyl halide was 1:0.5 or greater, and the effect of decreasing this ratio was not studied. In ether, however, the ratio was 1:0.82 and a yield of only 2.9 per cent was obtained.

The yield obtained with butyl bromide was 40.5 per cent, while yields of 66.6 and 80.5 per cent were obtained with butyl chloride. The dilution of the halide with petroleum ether may account for some of this difference, but it is believed that higher yields will be obtained with the butyl chloride, and this is in accord with evidence from the literature (25,26).

#### Preparation of Lithium Ethyl in Diethyl Ether.

The yield of lithium ethyl obtained in diethyl ether

was 1.8 per cent. Intense reaction occurred, but the reaction was marked by rapid evolution of gas and very little ether refluxing. This is typical of the Wurtz reaction and was probably due to the molar ratio of the lithium to ethyl bromide of 1:0.865. As the ratio should have been 1:0.5 for the reaction



the reaction was completed with the excess alkyl halide



thus giving the Wurtz reaction and a very low yield of lithium ethyl.

#### Preparation of Lithium Ethyl in Petroleum Ether.

In preparing lithium ethyl in petroleum ether molar ratios of lithium to ethyl bromide of 1:1.13, 1:1.37, and 1:1.34 were used. These ratios are all in the range above 1:0.5 and will give the Wurtz reaction if enough time is allowed. For example, in preparations in which only one half hour was allowed for the reaction, yields of 15.2 and 17.6 per cent were obtained; in a preparation in which one hour was allowed for reaction, a yield of only 1.7 per cent was obtained. Therefore, it may be assumed that this entire family of reactions proceeds faster in diethyl ether than in any of the other solvents used.

Preparation of Lithium Ethyl in Isopentane. The two preparations of lithium ethyl in isopentane gave yields of 18.4 per cent and 16.2 per cent. Increasing the time of reaction actually decreased the yield slightly as shown by a yield of 18.4 per cent at a run of three hours, and 16.2 per cent at a run of four hours. This decrease could not be due to the Wurtz reaction as in these runs the ratio of the lithium metal to ethyl bromide was kept at or below 1:0.5. It must be credited to experimental error.

Preparation of Lithium Methyl in Petroleum Ether. In reacting lithium metal with methyl iodide in petroleum ether to form lithium methyl no visible signs of reaction, such as cloudiness of solution, refluxing of ether, or formation of precipitate, were in evidence. Analysis of two of the above reactions gave yields of 3.2 per cent and zero per cent under similar conditions.

Preparation of Lithium Methyl in Diethyl Ether. Lithium methyl was prepared in diethyl ether by reacting lithium metal with methyl iodide. The reaction started with 30 seconds. The optimum time of reaction appeared to be one half hour; if the reaction proceeded beyond this, in the presence of excess methyl iodide, the yield would drop off due to the Wurtz reaction. The yield obtained under these

conditions was 43.1 per cent with a lithium metal to alkyl halide ratio of 1:1.1. Changing the ratio to 1:0.37 and letting the reaction proceed for one hour caused the yields to decrease to 24.4 and 22.6 per cent.

Reaction Between Lithium and Methyl Iodide

Without a Solvent. Lithium metal was placed in contact with methyl iodide without any ether solvent and no visible reaction occurred. Therefore, the diethyl ether must allow the methyl iodide to dissociate somewhat and the halogen then combines with the lithium metal.

Advantage of Lithium Wire. In the preparation of the lithium alkyls, lithium metal received in wire form is superior to that in chunk form, in that it can easily be cut directly into the reaction flask with scissors. The weight of metal used can be determined from the weight per unit length. The wire comes covered with a preservative grease that eliminates the need for keeping it under oil.

Coloration of Precipitates in Preparation of Lithium Alkyls. The precipitates of lithium halide formed as a by-product of the reaction



are generally colored grey, red, or purple. These

colors may be caused by colored organic by-products<sup>(25)</sup>. Also, in many cases, the reaction is characterized by the lithium metal changing color. In the case of lithium butyl and lithium ethyl, the lithium turns purplish-grey; in the case of methyl lithium, the metal turns gold.

Crystallization of Lithium Methyl From Solution.

Great difficulty arose in keeping the lithium methyl in solution for more than five to six hours as crystallization of the lithium alkyl would then begin. An attempt was made to prevent crystallization by constantly agitating the solution with a magnetic stirrer. However, the crystallization proceeded without any improvement. Once the crystals have formed, it is very difficult to redissolve them. The crystallization occurred in petroleum ether and diethyl ether to the same degree.

Analysis of Lithium Alkyls. The analysis of the lithium alkyl was based on the hydrolysis of the lithium alkyls to LiOH



followed by titration of the lithium hydroxide with standard hydrochloric acid. The errors in this analysis included the errors inherent in titration and weighing, plus the fact that the weighing was

performed on a highly volatile solvent, petroleum ether. Any ether that evaporated before the top was placed on the weighing bottle tended to concentrate the sample and make the analysis slightly higher than actual. It is estimated that the errors involved would be under five per cent.

Conductance of Lithium Alkyls. The conductance of the three lithium alkyl compounds in ether were too low for suitable electrolysis. The lowest in molecular weight in the series, lithium methyl, had the highest conductivity,  $1.16 \times 10^{-7} \text{ ohm}^{-1} \text{ cm}^{-1}$ . The lithium alkyl of the highest molecular weight tested was lithium butyl and it had the lowest conductivity,  $1.46 \times 10^{-8} \text{ ohm}^{-1} \text{ cm}^{-1}$ . When the alkyls were placed in petroleum ether, they had no effect on the original conductivity of the solvent, which was greater than the maximum that could be measured with the resistance box used,  $10^8$  ohms. The resistance of diethyl ether was also greater than  $10^8$  ohms.

Conductivity of Lithium Borohydride in Ether. The specific conductivity of a solution of lithium borohydride in diethyl ether was found to be  $1.52 \times 10^{-7} \text{ ohm}^{-1} \text{ cm}^{-1}$  for a concentration of 0.1 gram lithium borohydride per 50 milliliters of

diethyl ether. This rather low conductivity indicates that there is little dissociation of the lithium borohydride molecule in diethyl ether.

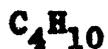
Effect of Addition of Lithium Borohydride to Lithium Alkyl Solution. When solid lithium borohydride was added to ether solutions of lithium alkyls there was no appreciable change in the resistance of the solutions. Apparently, there is no conductive complex formation between these two compounds.

Preparation of Grignard Reagent. The grignard compound, ethyl magnesium bromide, was prepared by reacting ethyl bromide with magnesium strips. The yield on the first preparation was 58.0 per cent, but this was increased to yields of 69.0, 70.0 and 71.9 per cent by slow, careful addition of the ethyl bromide. If equimolar quantities of reactants are used, the magnesium strips will usually all dissolve, but the highest yield obtained was 71.9 per cent. This indicates that side reactions decrease the yield.

Some of the reactions could be



followed by



or the alkyl halide could react with some of the grignard compound.



Effect of the Addition of Lithium Borohydride  
on the Resistance of the Grignard Solution in Ether.

When 0.11 grams of solid lithium borohydride was added to the 0.5 normal solution of ethyl magnesium bromide the resistance increased from 4760 ohms to 20,500 ohms in five minutes. This was accompanied by evolution of gas from the surface of the lithium borohydride. However, when 0.1 gram of lithium borohydride dissolved in 50 milliliters of ether was added to the grignard solution, the resistance decreased from 4760 ohms to 2350 ohms. Also the conductivity of the mixture was found to be  $6.16 \times 10^{-5} \text{ ohm}^{-1} \text{ cm}^{-1}$ , while the conductivity calculated, assuming colligative properties was  $3.35 \times 10^{-5} \text{ ohm}^{-1} \text{ cm}^{-1}$ . As the conductivity was higher than would be the case had the conductivities been merely additive, there is evidence of the formation of a conductive complex.

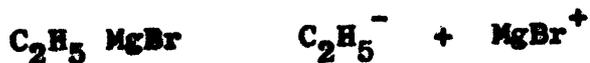
First Electrolysis. The first electrolysis of ethyl magnesium bromide in diethyl ether with lithium borohydride was designed to test the exit gases for boron and to isolate them if they contained boron. The data for this electrolysis are given in Table IX, page

Dry ice-methanol traps were placed in the exit gas line to trap any organo-boron compounds formed in the electrolysis. The compounds formed should have a boiling point above  $-80^{\circ}\text{C}$ , the temperature of the traps. At the end of the electrolysis, five to ten milliliters of liquid were contained in each trap. However, the liquid gave a negative test for boron, and boiled at the boiling point of ether,  $35^{\circ}\text{C}$ . Therefore, it is assumed that it was diethyl ether that boiled through the reflux condenser into the traps.

Reduction of Permanganate. The passage of the exit gases through the permanganate solution caused a five per cent reduction in 200 milliliters of a 0.075 normal solution of potassium permanganate. If ethylene had been evolved in the electrolysis it would have passed through the traps, and could have caused the reduction in the permanganate solution. Therefore, there was no proof of a boron compound, as an unsaturated hydrocarbon could have caused the reduction.

Second Electrolysis. The purpose of the second electrolysis was to determine whether the reducing exit gases contained boron. The conditions were similar to those in the first electrolysis, as shown in Table IX, page 76.

Increasing Current. After the first six hours of electrolysis, the current began to rise slowly from the original 0.040 ampere. The current rose slowly at first, then more rapidly. From the twelfth hour of electrolysis to the fourteenth hour, the current rose from 0.140 ampere to 0.200 ampere. This can be explained by the following mechanism. Ethyl magnesium bromide ionized



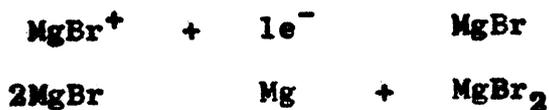
at the anode the ethyl radical is discharged



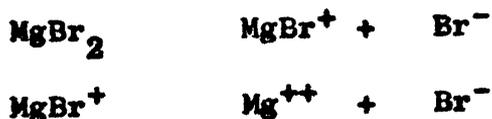
followed by



while at the cathode



The magnesium bromide which is ether soluble, can ionize



and the addition of the more salt like compound, magnesium bromide, to the solution would cause the current to rise as it is formed.

Gas Evolution. Gas was evolved during the first part of the electrolysis, but after six hours no more gas was given off. This could be explained by the above reaction in which the current would begin to be carried by the magnesium bromide ions rather than the ionized grignard compound.

Water Bubbler. The water in the bubbler through which the exit gas had been bubbled gave no test for boron when analyzed with turmuric. This means that there were no boron-containing gases given off.

Benzene Extraction. The transfer of the electrolyzed material from ether to benzene was to test for the formation of any liquid or solid organo-boron compounds. Since the lithium borohydride was found to be insoluble in benzene by an active hydrogen test, any test for boron from the solution would come from any organo-boron compound formed. However, there was no test for boron, although the solution gave off gas when hydrolyzed. It is believed that the gas is ethane given off in the hydrolysis of dissolved ethyl magnesium bromide.



The amount of unreacted ethyl magnesium bromide in the benzene solution based on the gas evolved is 0.040 mols

which means that 66 per cent of the grignard reagent has been used up.

Ether Extraction. The purpose of the ether extraction was to determine the amount of lithium borohydride left after electrolysis and to purify the cathode deposit. The ether naturally gave the test for boron, as it contained lithium borohydride, and contained 37.6 mols of active hydrogen per gram of solution. Therefore, 1.38 grams of lithium borohydride were left unreacted after electrolysis.

Cathode Deposit. The grey flaky cathode deposit after being washed with ether, benzene, and methyl alcohol was insoluble in water and reacted rapidly with dilute hydrochloric acid, dissolving and giving off gas. When the solution was made basic, a white precipitate formed. This data, plus evidence from the literature<sup>(1)</sup>, indicates that magnesium is the cathode deposit.

### Recommendations

Upon completing the experimental work on this investigation, the following recommendations are made for future study.

Lithium Alkyl Production. It is recommended that attempts be made to prepare lithium alkyls at lower

temperatures, 0°C - 10°C. A low temperature preparation may increase the yields of these compounds (20).

Zinc Diethyl. It is recommended that the solubility of sodium and lithium borohydride in diethyl zinc be determined. Also, it is recommended that the reactivity of lithium and sodium borohydride with diethyl zinc be determined to evaluate diethyl zinc as a possible solvent for electrolysis.

Sodium Borohydride - Sodium Methyl - Zinc Diethyl System. It is recommended that the system sodium borohydride - sodium methyl - zinc diethyl be studied and electrolyzed, if there is no reaction between sodium borohydride and zinc diethyl.

Solubility of Lithium Borohydride. It is recommended that the solubility and conductivity of lithium borohydride be determined in various amines, polyethers, and tetrahydrofuran to evaluate them as possible solvents for electrolysis.

Reaction Rates. It is recommended that the rate of reaction of lithium methyl and ethyl with the low molecular weight amines be determined. If the rate of reaction is relatively slow, they could be used as solvents for electrolysis.

### Limitations

The limitations imposed upon this investigation are presented in this section.

The solvents in which the conductivity measurements were made was diethyl ether and petroleum ether. The metal alkyls studied in this investigation were lithium methyl, ethyl, and butyl. The only grignard compound studied was ethyl magnesium bromide. The systems electrolyzed were solutions from 0.366 normal to 0.395 normal in ethyl magnesium bromide and contained 2.5 grams of lithium borohydride in 300 milliliters of diethyl ether. The electrolyses were performed only at 35°C.

Electrolyses were carried out for three hours at 0.075 ampere and 14 hours at 0.04 to 0.200 ampere. The only cathode material used was mercury and the only anode material was platinum with a surface area of one square inch. The diethyl ether used was dried with sodium hydride.

## V. CONCLUSIONS

The experimental work on the preparation of lithium methyl, lithium butyl, lithium ethyl and ethyl magnesium bromide and the electrolytic study of solutions of these compounds in diethyl ether led to the following conclusions.

1. The specific conductances of 0.15 to 0.21 molar solutions of lithium methyl, lithium ethyl, and lithium butyl in diethyl ether at 25°C are less than  $1.61 \times 10^{-7} \text{ ohm}^{-1} \text{ cm}^{-1}$ .

2. The specific conductance of a 0.5 molar solution of ethyl magnesium bromide in diethyl ether at 25°C is  $3.08 \times 10^{-5} \text{ ohm}^{-1} \text{ cm}^{-1}$ .

3. Analysis indicated that the cathode product of the electrolysis of 0.35 to 0.4 molar solution of ethyl magnesium bromide with a 0.37 molar solution of lithium borohydride in diethyl ether between a mercury cathode and a platinum anode at a current density of from 0.00066 to 0.0033 amperes per square decimeter, at a temperature of 35°C, is magnesium.

4. The addition of a 0.11 to 0.13 gram of lithium borohydride to a 0.15 to 0.21 molar solution of lithium methyl, lithium ethyl, or lithium butyl

causes less than a 15 per cent change in their conductances, at a temperature of 25°C.

5. A saturated solution of lithium borohydride in benzene contains less than 0.011 milliatoms per gram of solution.

6. In the electrolysis of ether solutions of 0.35 to 0.40 molar ethyl magnesium bromide and 0.37 molar lithium borohydride between a mercury cathode and a platinum anode at an anode current density of 0.0062 to 0.031 amperes per square decimeter, organo-boron compounds are not produced.

7. Lithium methyl cannot be prepared in petroleum ether by the reaction of methyl iodide on lithium metal at 35°C with a solvent to alkyl halide ratio of 1.5 grams to one, in yields exceeding three per cent.

8. Lithium ethyl can be prepared in yields of 15 to 18 per cent in petroleum ether and isopentane at 35°C with an isopentane to alkyl halide ratio of 10 grams to one and a petroleum ether to alkyl halide ratio of 1.3 grams to one, by the reaction of ethyl bromide on lithium metal.

9. Lithium methyl can be prepared in yields of 22.6 to 43.1 per cent in diethyl ether at 35°C, by the action of methyl iodide on lithium metal.

10. Lithium butyl can be prepared in yields of 66.6 to 80.2 per cent in petroleum ether, at 35°C with a solvent to alkyl halide ratio of 1.7 grams to one, by the action of butyl chloride or butyl bromide on lithium metal.

11. There is no apparent reaction between lithium borohydride and ethyl magnesium bromide in diethyl ether at 25°C.

12. There is no apparent reaction between lithium borohydride and the lithium alkyl in diethyl ether at 25°C.

## VI. SUMMARY

The purpose of this investigation was to study the electrochemical properties of solutions of lithium methyl, ethyl, and butyl with lithium borohydride in diethyl ether and to electrolyze ethyl magnesium bromide with lithium borohydride in ether between a mercury cathode and a platinum anode.

A survey of the literature was conducted for information on the preparation of the lithium alkyls, the electrolysis of the grignard reagent, the chemical properties of these compounds and lithium borohydride, and the nature of free radical reactions. Information was discovered which proved very helpful in the investigation, but no mention was found of a dual anodic free radical reaction such as the expected borane-hydrocarbon free radical reaction.

Lithium ethyl was prepared from ethyl bromide and lithium in petroleum ether and isopentane in yields of 15 to 18 per cent. Lithium butyl was prepared from butyl chloride or butyl bromide in petroleum ether in yields of 66 to 85 per cent. Lithium methyl was prepared from methyl iodide and lithium metal in dry diethyl ether, in yields of 22 to 43 per cent. These compounds were transferred

to diethyl ether and their conductivities were found to be less than  $1.61 \times 10^{-7} \text{ ohm}^{-1} \text{ cm}^{-1}$  with and without added lithium borohydride.

Ethyl magnesium bromide was then prepared from ethyl bromide and magnesium metal in diethyl ether. The conductivity of this compound was measured in diethyl ether with lithium borohydride, and was found to be  $3.08 \times 10^{-5} \text{ ohm}^{-1} \text{ cm}^{-1}$ .

Electrolyses were performed on 300 milliliters of ethyl magnesium bromide solutions, 0.366 and 0.395 molar, containing 2.5 grams of lithium borohydride. The electrolyses were performed between a mercury cathode and a platinum anode, with magnetic agitation. The apparatus was constructed from glassware.

Two tests were made, the first an attempt to isolate any volatile organo-boron compound, and to test for the presence of any boron compound boiling below  $-80^{\circ}\text{C}$ , the temperature of the dry-ice methanol traps. In this electrolysis, it was found that the volatile products of the electrolysis would reduce a permanganate solution slightly; however, the gases passed through the dry-ice methanol traps without condensing.

The second electrolysis was performed to determine if the reducing exit gases contained boron, and to

determine if additional time of electrolysis affected the products. The exit gases were bubbled through water and the water tested for the borate ion with a solution of turmeric in alcohol. During the 14 hours of electrolysis, the current increased from 0.04 ampere to 0.2 ampere, the increase becoming noticeable after the sixth hour of electrolysis. Also, after six hours gases ceased to be evolved from the electrolysis and magnesium was plated out at the cathode.

It was found that the exit gases contained no boron, and then the body of the solution was transferred to benzene, in which lithium borohydride was found to be insoluble. This solution was then tested for boron. As the solution also gave no test for boron, it is believed that the ethyl free radical is formed at the anode alone for the first part of the electrolysis, and disproportionates to form ethane and ethylene. As the electrolysis continues, the concentration of magnesium bromide is increased in the solution, causing the current to increase and the bromide ion to be discharged at the anode.

VII. BIBLIOGRAPHY

1. Arnold, H. R.: Process for Producing Organo-Boron Compounds, U. S. Pat. 2,402, 589 (June 25, 1946); C. A., 40, 5769 (1946).
2. Bauer, S. H.: Structures and Physical Properties of the Hydrides of Boron and of Their Derivatives, Chem. Revs., 31, 43-75 (1942).
3. Brockman, C. J.: "Electro-Organic Chemistry", pp. 23-45, John Wiley and Sons, New York, N. Y., (1926)
4. Brown, A. C. and J. Walker: Elektrolytische Synthesen Zweibasischer Sauren, Ann., 261, 107 (1891); Brockman, C. J., "Electro Organic Chemistry", p. 33. John Wiley and Sons, New York, N. Y., (1926)
5. Bryce - Smith, D., and E. E. Turner: Organo-metallic Compounds of the Alkali Metals. Part II. The Metallation and Dimetallation of Benzene, J. Chem. Soc., 861-867 (1953).
6. Cason, J.: Branched Chain Fatty Acids. IV. A Further Study of the Preparations of Ketones and Keto Esters by Means of Organo-Cadmium Reagents, J. Am. Chem. Soc., 68, 2078 (1946).
7. Cason, J.: The Use of Organo-Cadmium Reagents for the Preparation of Ketones, Chem. Revs., 40, 15-30 (1947).
8. Cramer, P. L.: The Decomposition of Tetraethyl Lead Into Ethylene and Hydrogen in Benzene Solution, J. Am. Chem. Soc., 56, 1234, (1934).
9. Evans, W. V., and David Braithwaite; The Electrolysis of n-Propyl Magnesium Bromide and Isopropyl Magnesium Bromide in Diethyl Ether, J. Am. Chem. Soc., 61, 898 (1939).
10. Evans, W. V., and Edmund Field: Electrolysis of Methyl Magnesium Halides in Ether Solution, J. Am. Chem. Soc., 58, 720 (1936).

11. Evans, W. V., and Edmund Field: Electrolysis of Methyl Magnesium Iodide in n-Butyl Ether, J. Am. Chem. Soc., 58, 2284 (1936).
12. Evans, W. V., and F. H. Lee: Electrolysis of Ether Solutions of the Grignard Compound. Isolation, Identification, and Quantitative Determination of Anodic Products, J. Am. Chem. Soc., 56, 654 (1934).
13. Evans, W. V., and J. M. Nelson: The Electromotive Force Developed in Cells Containing Non-aqueous Liquids, J. Am. Chem. Soc., 39, 82 (1917).
14. Evans, W. V., R. Pearson and David Braithwaite: The Electrolysis of Aryl Magnesium Bromides in Diethyl Ether: The Behavior of Short Lived Aryl Free Radicals, J. Am. Chem. Soc., 63, 2574 (1941).
15. Frankland, E., Uber die Isolirung der Organische Radicale, Ann. 71, 171 (1849); Gilman, H.: "Organic Chemistry", p. 490. John Wiley and Sons, New York, N. Y. (1947).
16. Garzuly-Janke, R.: Regularities in the Organic Metallic Compounds, J. Pract. Chem. 142, 141 (1936); C. A., 29, 2910 (1935).
17. Gilman, H.: "Organic Chemistry", pps. 490-552. John Wiley and Sons, New York, N. Y. (1947).
18. Gilman, H. and L. D. Apperson: Reactions Between Organo-lead Compounds and Some Metallic Halides, J. Org. Chem., 4, 162 (1934).
19. Gilman, H. and J. C. Barke: Relative Reactivities of Organo-Metallic Compounds. XXI. Organo-lead Radicals and Derivatives, J. Am. Chem. Soc., 61, 731 (1939).
20. Gilman, H., J. A. Beel and C. G. Branner: The Preparation of n-Butyl Lithium, J. Am. Chem. Soc., 71, 1499 (1949).
21. Gilman, H. and A. H. Haubein: The Quantitative Analysis of Alkyl Lithium Compounds, J. Am. Chem. Soc., 66, 1515 (1944).

22. Gilman, H., Wright Langham and Fred W. Moore: Some Interconversion Reactions of Organo-Lithium Compounds, *J. Am. Chem. Soc.*, 62, 2327 (1940).
23. Gilman, H. and F. W. Moore: Some Factors Affecting Halogen-Metal Interconversion, *J. Am. Chem. Soc.*, 62, 1843 (1940).
24. Gilman, H. and L. A. Woods: A Color Test for Some Highly Reactive Organo-Lithium Compounds, *J. Am. Chem. Soc.*, 65, 33 (1943).
25. Gilman, H., E. A. Zoellner and W. M. Selby: The Yields of Some Organo-Lithium Compounds by the Improved Procedure, *J. Am. Chem. Soc.*, 55, 1252 (1933).
26. Gilman, H., E. A. Zoellner and W. M. Selby: An Improved Procedure for the Preparation of Organo-Lithium Compounds, *J. Am. Chem. Soc.*, 54, 1957 (1932).
27. Goddum, L. W. and H. E. French: The Electrolysis of Grignard Solutions, *J. Am. Chem. Soc.*, 49, 1295 (1927).
28. Goubeau, J.: Compounds of Semi-Metals With Non-Metals, *Fiat Review of German Science, Inorganic Chemistry, Part I*, pps. 215-238. Translated by Dr. Nelson F. Murphy, *C. A.* 43, 2105 (1949).
29. Greenhalgh, C. W. and H. B. Heubest: Reaction Between 17-Keto Steroids and Organo-Metallic Compounds, *J. Chem. Soc.*, 1190 (1951).
30. Haubein, A. H.: Solvents in Organo-Metallic Chemistry, *Iowa State Coll. J. Sci.*, 18, 48 (1943).
31. Hein, F.: Salt Nature of Sodium Ethyl: Indirect Electrolysis of Zinc Diethyl, *Z. Electrochem.*, 28, 469 (1922).
32. Hein, F., E. Petzcher, K. Wagler and F. A. Segitz: Salt-like Behavior of Alkali Alkyls in Metal Alkyls as Solvents, *Z. anorg. allgem. Chem.*, 141, 161 (1924); *C. A.* 19, 1080 (1925).

33. Hein, F., and H. Pauling: Conductivity and State of Electrolyte in Metallic Alkyls, Z. Physic. Chem. A, 165, 338-366; C. A. 17, 670 (1923).
34. Hein, F. and H. Schramm: Properties of Zinc Ethyl, Z. Physic. Chem., Abt. A, 149, 408-416 (1930); C. A. 24, 5207 (1930).
35. Hein, F. and H. Schramm: New Investigations Concerning Alkali Alkyls, Z. Physic. Chem., Abt. A, 151, 234-256 (1930); C. A. 25, 861 (1931).
36. Hein, F., and A. Segitz: The Nature of Metallic Alkyls, Z. anorg. allgem. Chem. 158, 153 (1926); C. A. 21, 891 (1927).
37. Hofferth, B. F.: Some Organo-Metallic Compounds Containing Reactive Functional Groups, Iowa State Coll. J. Sci. 26, 219-221 (1952); C. A. 47, 8672 (1953).
38. Hurd, D. T.: Reaction of Diborane With the Hydrocarbons, J. Am. Chem. Soc., 70, 2053 (1948).
39. Karrer, P.: "Organic Chemistry", p. 156, Elsevier Publishing Company, Inc., New York, N. Y., 1950.
40. Kassel, L. S.: The Thermal Decomposition of Methane, J. Am. Chem. Soc., 54, 3949 (1932).
41. Laurent, A.: Benzoyl, Am., 5, 397 (1835); Rice, F. O. and K. K. Rice: "Aliphatic Free Radicals", p. 21. Johns Hopkins Press, Baltimore, 1935.
42. Leermakers, J. A.: The Effect of Ethyl Radicals on the Thermal Decomposition of Azomethane, J. Am. Chem. Soc., 55, 4508 (1933).
43. Liebig, J.: Ueber die Constitution des Aethers and seiner Verbindungen, Ann. 9, 1 (1834); Rice, F. O., and K. K. Rice: "Aliphatic Free Radicals", p. 21. Johns Hopkins Free Press, Baltimore, 1935.

44. Liebig, J. and Wohler: Benzoyl and Benzoesaure, Ann. 3, 282 (1832); Rice F. O. and K. K. Rice; "Aliphatic Free Radicals", p. 21. Johns Hopkins Press, Baltimore, (1935)
45. Long, L. H., and R. G. W. Norrish: Strengths of Certain Covalent Metallic Bonds, Trans. Roy. Soc. London, A241, 587 (1949); C. A. 43, 5242 (1949).
46. Maryel, C. S., F. D. Hager and D. D. Coffman: The Mechanism of the Reaction Between Lithium, n-Butyl and Various Organic Halogen Compounds, J. Am. Chem. Soc., 49, 2323 (1927).
47. Noller, C. R.: The Preparation of Zinc Alkyls and Their use in the Synthesis of Hydrocarbons, J. Am. Chem. Soc., 51, 594 (1929).
48. Paneth, F., and W. Hofeditz: Preparation of Free Methyl, Ber., 62, 1335 (1929).
49. Paneth, F., and W. Lautsch: Free Organic Residues in The Gaseous State (II) Free Ethyl III. Reactions of the Free Radicals, Ber., 64, 2702 (1931).
50. Perkins, W. H., and F. S. Kipping: "Organic Chemistry", pps. 224-228. W. & R Chambers, Ltd., London (1922).
51. Perine, T. D., and H. Rappaport: Preparation of Organo-Lithium Compounds, Anal. Chem. 20, 635-6 (1948).
52. Rice, F. O.: Decomposition of Organic Compounds Into Free Radicals, Trans. Faraday Soc., 30, 152-69 (1934); C. A. 28, 2319, (1934).
53. Rice, F. O. and K. F. Herzfeld: The Thermal Decomposition of Organic Compounds From the Standpoint of Free Radicals VI. The Mechanism of Some Chain Reactions, J. Am. Chem. Soc., 56, 284 (1934).
54. Rice, F. O. and K. K. Rice: "Aliphatic Free Radicals", pps. 69-92. Johns Hopkins Press, Baltimore, (1935).

55. Schechter, W. H., R. M. Adams, and C. B. Jackson: Boron Hydrides and Related Compounds, pps. 28-606, Callery Chemical Co., (1951).
56. Schlenk, W. and Johanna Holz: Uber die Einfachsten Metallorganischen Alkaliverbindungen, Ber., 50, 271 (1917).
57. Schlesinger, H. I., and A. B. Burg: Recent Developments in the Chemistry of the Boron Hydrides, Chem. Revs. 31, 1 (1942).
58. Schlesinger, H. I., and H. C. Brown: Lithium Borohydride, J. Am. Chem. Soc., 62, 3429 (1940).
59. Snyder, H. R., J. A. Kuck and J. R. Johnson: Organo-Boron Compounds and a Study of Their Reaction Mechanism, J. Am. Chem. Soc., 60, 105 (1938).
60. Spencer, J. F., and G. M. Price: The Action of Calcium and Lithium on Organic Halides, J. Chem. Soc., 97, 385 (1910).
61. Talaleava, T. V., and K. A. Kocheshkov: New Methods for the Preparation of Crystalline Lithium-Organic Compounds of Aliphatic, Alkaryl, and Aromatic Series, Doklady Akad. Nauk. S. S. S. R., 77, 621 (1951); C. A. 45, 10191 (1951).
62. Talaleava, T. V., and K. A. Kocheshkov: New Methods for the Preparation of Crystalline Lithium Ethyl, Zhur. Obshchei Khim. 23, 392 (1953); C. A. 48, 3245 (1954).
63. Tang, P. J.: "The Reaction of Monochloromethyl Ether With Organo-Metallic Compounds", Unpublished M. Sc. Thesis, Library, Va. Poly. Inst., Blacksburg, Va. (1953).
64. Taylor, H. S. and W. H. Jones: The Thermal Decomposition of Metal Alkyls in Hydrogen - Ethylene Mixtures, J. Am. Chem. Soc., 52, 1111 (1930).
65. Thompson-Houston Co. Ltd.: Process for Preparing Alkylated Boron Compounds, British Pat. 618,358 (Feb. 21, 1949); C. A. 43, 6221 (1949).

66. Tinsley, R. S.: A Review on the Literature on the Electrolysis of Grignard Reagents in Ether Solution, Unpublished report submitted to Dr. Nelson F. Murphy, Va. Poly. Inst. (1954).
67. Truce, W. E. and F. M. Amos: Metalation of Diaryl Sulfones, J. Am. Chem. Soc., 68, 2133 (1946).
68. Whitmore, F. C.: "Organic Compounds of Mercury", pps. 221-226, Chem. Cat. Co. Inc., New York. (1921).
69. Whitmore, F. C.: "Organic Chemistry", pps. 447-429, D. Van Nostrand Co., New York, (1951) 2nd Ed.
70. Wiberg, E., and W. Ruschmann: Preparation of Alkyl Borides of the type  $BR_3$ , Ber., 70 B, 1583 (1937); C. A. 31, 6613, (1937).
71. Wittig, G., and M. Leo: Polarisability of the  $C_2H_4$  Anion, Ber. 64, 2395 (1930).
72. Wooster, C. B.: Organoalkali Compounds, Chem. Revs. 11, 1 (1932).
73. Ziegler, K.: The Importance of Alkali Metal Organic Compounds for Synthesis, Angew. Chem., 49, 455 (1936); C. A. 30, 6325 (1936).
74. Ziegler, K.: Organic Alkali Metal Compounds, Ger. Pat. 487,727 (Dec. 10, 1927); C. A. 24, 2138 (1930).
75. Ziegler, K.: Organic Compounds of Lithium, Ger. Pat. 512,822 (Oct. 15, 1929); C. A. 25, 2154 (1931).
76. Ziegler, K.: Problems and Results of the Newer Investigations of Free Radicals, Z. Angew. Chem., 43, 915 (1930).
77. Ziegler, K., and H. Colonius: Alkali Organic Compounds (V) Suitable Synthesis of Simple Lithium Alkyls, Ann. 479, 123 (1930); C. A. 24, 3777 (1930).

78. Ziegler, K., F. Crossman, H. Kleiner, and  
O. Schafer: Alkali Organic Compounds (1)  
Reaction Between Unsaturated Hydrocarbons  
and Alkali Metal Alkyls, Ann. 473, 1 (1929);  
C. A. 23, 5181 (1929).
79. Ziegler, K. and H. G. Gilbert: Organo Alkali  
Compounds, Ann., 567, 179 (1950); C. A. 44,  
7757 (1950).

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